# THE FOUNDATIONS OF CHEMICAL KINETICS

E.N. YEREMIN



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#### Е.Н. ЕРЕМИН

## ОСНОВЫ ХИМИЧЕСКОЙ КИНЕТИКИ

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#### **Preface**

This textbook has emerged from the lectures on chemical kinetics given by the author for more than 15 years for chemistry students at the Moscow State University as part of a general course in physical chemistry. Much space in the book is devoted to the fundamental concepts and therefore it may serve as an elementary textbook. On the other hand, the book provides a more detailed treatment of some theoretical problems than is found in ordinary courses of physical chemistry. Thus, the section dealing with unimolecular reactions has been considerably augmented; an example is a detailed account of the Slater theory.

Furthermore, the author has found it useful to supplement the treatment of the various aspects of the theory of the activated complex (transition-state theory) with concrete examples of the application of this theory to bimolecular reactions involving complexes of various configurations, the results of calculations being compared with the theory of activated collisions. This information must be helpful in applying the theory of kinetics in practical work. The exposition of the principles of transition-state theory is preceded by Chapter 5 which is devoted to the foundations of statistical thermodynamics. The experience of teaching physical chemistry at the Chemistry Department has shown that this chapter may be self-contained in a study of the fundamentals of thermodynamics.

Separate chapters are concerned with the kinetics of photochemical reactions and reactions taking place in electrical discharges. The inclusion of these topics may evidently be partly explained by the author's personal tastes and the trend of his work in the corresponding fields of chemical kinetics.

Reactions in solutions and homogeneous catalysis in solutions are treated in Chapter 12. Here much attention is paid to the theory of intermediates and, in particular, to the classical works of E. I. Shpitalsky, a Professor of Moscow University.

The author has deliberately avoided expounding heterogeneous catalysis, an area so wide that it would have increased the size of the book three times at least, among other things.

The book is intended both for a beginning student of chemical kinetics at chemistry and chemical-engineering higher schools and for a more thorough study of the subject. It may be found useful by post-graduates and also by all those who wish to study chemical kinetics.

In preparing this second edition I have taken into account all the comments made by my colleagues; also, all the misprints have been corrected and I have included a new section devoted to methods of measurement of reaction rates and of determination of reaction order and also chapters on the kinetics of topochemical processes.

In conclusion, the author extends his sincere thanks to E. A. Rubtsova and V. M. Belova who have been kind enough to offer their help in preparing this manuscript.

E. N. Yeremin

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#### CHAPTER 1

### Basic Concepts and Empirical Relationships

Physical chemistry is concerned with study of chemical systems (i. e., systems in which chemical reactions take place) mainly from the standpoint of thermodynamics and kinetics. The thermodynamic treatment based on the study of the energetic properties of a system and its entropy allows one to determine the possible final result of a chemical interaction. Very often the conclusion made as to the possibility of a reaction does not mean that the chemical reaction of interest to us will really be accomplished under given conditions. For example, a thermodynamic study of the system

C (graphite) → C (diamond)

that is, the transformation of one crystalline modification of carbon (graphite) into another modification, diamond, shows that under ordinary conditions (298.15 K and 1 atm) graphite is more stable than diamond, i.e., that there exists the following inequality of the chemical potentials:

$$\mu_{\text{grap}^{i_0}} < \mu_{\text{diam}} \tag{1.1}$$

and there must occur a spontaneous transformation of diamond into graphite. We know, however, that this is not the case in actuality. Such a contradiction between theoretical inferences and practical observations is associated with the limitedness of the thermodynamic method which is concerned only with the initial (graphite) and final (diamond) states of the system. Indeed, under ordinary conditions the molar free energy of graphite is lower than the free energy of diamond. These energy relations may be explained graphically (Fig. 1.1).

The point, however, is that the real process of recrystallization, i.e., the conversion of a crystal lattice of the diamond type into that of the graphite type involves of necessity certain intermediate steps. The formation of intermediate structures, which originally constituted the distorted lattice of diamond, is associated with the consumption of energy amounting to  $G^{\neq}$ . Therefore, the actual

change of the energy during the course of the process will be depicted by a curve with a maximum. The height of the maximum as compared with the energy of the original configuration (diamond),  $\Delta G^{\neq}$ , may be called the free energy of activation.

In other words, the thermodynamically possible transition of the system from the initial to the final state requires that a certain energy barrier be overcome, a barrier that hinders the real occurrence of the process, especially at low temperatures. At higher temperatures, the atoms in the crystal lattice move more rapidly and have more energy, and therefore the attainment of

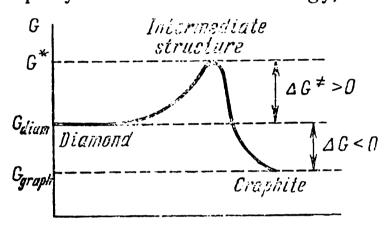


Fig. 1.1. Changes in the Gibbs free energy during the transformation of diamond to graphite at 298.15 K and I atm (an arbitrary scale).

the intermediate configuration—the passage over the energy barrier—is facilitated. Indeed, at sufficiently higher temperatures diamond turns spontaneously into graphite.

From the foregoing it must be clear that thermodynamics, which does not deal with intermediate states and is concerned only with comparing the initial and final

states, can provide no information about the actual feasibility of a thermodynamically possible process.

Returning to the thermodynamic method of investigation, it is possible to find conditions for the equilibrium coexistence of graphite and diamond; they are known to be characterized by the equality of the chemical potentials:

$$\mu_{\text{graph}} = \mu_{\text{diam}} \tag{1.2}$$

At a temperature of 298.15 K (according to an approximate calculation), it will suffice to compress graphite up to 15,000 atm. Beginning from this point, the spontaneous transformation of graphite into diamond becomes possible. But even at higher pressures when

$$\mu_{\rm graph} > \mu_{\rm diam} \tag{1.3}$$

the process does not take place at all or proceeds at such a slow rate that it is practically impossible to detect the appearance of the diamond structure. The cause of this lies in the same difficulty of surmounting the energy barrier at low temperatures. Recrystallization proceeds easily at high temperatures, of the order of 2000 K, but under these conditions the inequality (1.3) necessary

for the formation of diamond requires a considerably higher pressure (more than 45,000 atm).

Thus, thermodynamics makes it possible to judge, on the basis of the energetic properties of a system and its entropy, about the possible final outcome of a chemical interaction, about the state of equilibrium. But it furnishes no information on the time period required for this result to be attained.

The time factor, a very important quantity in practice, is left out of an ordinary thermodynamic treatment. On the other hand, the occurrence of processes in time is the concern of the thermodynamics of non-equilibrium processes (see Chapter 14).

Many examples could be cited, in which thermodynamically possible processes do not practically occur because of negligibly low rates. Thus, the reaction between hydrogen and oxygen

$$2H_2 + O_2 \longrightarrow 2H_2O$$

is accompanied by a great loss of free energy:

$$\Delta G_{298}^0 = -109.0$$
 kcal

At room temperature the equilibrium shifts almost completely to the side of formation of water. It is known, however, that the oxyhydrogen gas may stand for an indefinite period of time without the noticeable formation of water. The point here again is a high energy barrier, the necessity to consume a high amount of energy for the intermediate states to be formed. But as soon as a catalyst (sponge platinum) is introduced into the oxyhydrogen gas, the reaction will occur with a very high velocity, with an explosion.

It is therefore clear that the study of chemical systems from a thermodynamic standpoint alone is insufficient. No less important is their study from the viewpoint of the rates of processes, from the standpoint of kinetics, which is thus of great practical importance since it determines the feasibility of various chemical reactions, the fundamental possibility of which has been established thermodynamically.

Secondly, kinetics is of great theoretical importance since it allows one to get a deeper insight into the mechanism of reactions, i.e., to determine, more or less reliably, the intermediate reaction steps on the way to the end product. Thus, the study of kinetics of the formation of water shows that in the first stages there appear free atoms and radicals which are chemically highly active and readily enter into further conversions:

(1) the appearance of a free hydroxyl group:

$$H_2 + O_2 \longrightarrow 2OH$$

(2) the dissociation of the hydrogen molecules upon collision with a particle:

$$H_2 + M \longrightarrow H + H + M$$

(3) the formation of ozone and an oxygen atom:

$$O_2 + O_2 \longrightarrow O_3 + O$$

All these processes require a large quantity of energy (for example, for the dissociation of  $H_2$  to take place, 103.5 kcal/mole of  $H_2$  is required); the occurrence of these processes generates the reaction. This energy is consumed on surmounting the main energy barrier.

The activated particles formed in stages (1), (2) and (3) interact with bond-saturated molecules. These are the processes that continue and accelerate the reaction:

(1) 
$$OH + H_2 \longrightarrow H_2O + H$$

(2) 
$$H + O_2 \longrightarrow OH + O$$

(3) 
$$O + H_2 \longrightarrow OH + H$$

Finally, an important part is played by processes in which the active particles perish, as a result of which the reaction may be brought to completion without an explosion.

A distinction is made between the processes in which atoms and radicals are destroyed at the walls of the reaction vessel:

(4) 
$$H + H + wall \longrightarrow H_2 + wall$$

(5) 
$$OH + H + wall \longrightarrow H_2O + wall$$

and those in which they are destroyed in the bulk:

$$(6) 11 + O_2 + M \longrightarrow HO_2 + M$$

The last equation should be considered in more detail. It describes the reaction during the course of a triple collision, i.e., a collision of three particles (also called a ternary or three-body collision): a hydrogen atom, an oxygen molecule and a third particle (a molecule), the participation of which is necessary for the stabilization of the newly formed molecule—the radical HO<sub>2</sub>, by way of removal of the energy.

It is interesting that the formation of the free radical HO<sub>2</sub> was originally postulated with the purpose of explaining some of the observed specific features of the oxidation of hydrogen. The activity of the particle HO<sub>2</sub> was assumed to be low since only in isolated cases does it continue the reaction; its formation mainly implies the removal of a considerably more active particle—the hydrogen atom. The formation and existence of the free radical HO<sub>2</sub> was later confirmed by direct experimental observations. Thus, the discovery of the radical HO<sub>2</sub> was made as if at the tip of the pen.

#### 1.1. Basic Concepts and Definitions

Let us first define the rate of a reaction. The rate of a reaction in gas mixtures and in liquid solutions is defined as **the rate of change of the amount of one of the reactants or products per unit volume per unit time.** The change of the quantity of a given substance in the system per unit time may be expressed by the derivative dN/dt, where N is the number of moles of the substance and t is the time. If we denote the volume of the system by V, then the instantaneous (true) rate \* will be defined by the following relation:

$$w = \pm \frac{1}{V} \cdot \frac{dN}{dt} \tag{1.4}$$

In this expression the plus sign applies to products since their concentration increases with time; the minus sign is used for reactants because their concentration decreases with increasing time. Thus, the rate of reaction is always positive. Expression (1.4) is a strict definition of the reaction rate, which is applicable in a general case and for a system of variable volume. A simpler equation, however, is often used, which is suitable for a reaction in a system of constant volume. Since the ratio N/V=c, i.e., is equal to the concentration of the substance (its molarity), then at constant volume

$$w = \pm \left(\frac{dc}{dt}\right)_{V} \tag{1.5}$$

In this, simpler definition the reaction rate (at constant volume) is the *change* of the concentration of a given reactant or product in unit time. Equation (1.5) is evidently applicable to reactions in solutions without substantial reservations; it also applies to reactions involving gases provided that they take place in closed reaction vessels. With the volume being kept constant, expression (1.5) can be even more simplified:

$$w = \pm \frac{dc}{dt} \tag{1.6}$$

It is necessary to note that if the reaction taking place in a system involves several substances, for example, A, B, D, ..., E, F, that is,

$$v_1A + v_2B + v_3D + \dots \longrightarrow v_1'E + v_2'F + \dots$$
 $c_1 \quad c_2 \quad c_3 \quad c_1' \quad c_2'$ 

(where  $c_i$ s are the reactant concentrations at various elapsed times), then for the reaction rate to be determined unambiguously it will suffice to trace out the change in concentration of one of the reactants. The changes in the concentrations of the other

<sup>\*</sup> In contrast to the so-called average rate.

reactants can always be found from the ratios of the stoichiometric coefficients  $v_i$ .

Thus, for example, the rate for the reactant A

$$w = -\frac{dc_1}{dt}$$

is related to the rates with respect to the other reactants by the equation:

$$w = -\frac{dc_1}{dt} = -\frac{v_1}{v_2} \cdot \frac{dc_2}{dt} = -\frac{v_1}{v_3} \cdot \frac{dc_3}{dt} = \dots = \frac{v_1}{v_1'} \cdot \frac{dc_1'}{dt} = \dots$$
(1.7)

## 1.2. The Basic Law of Kinetics. Effect of Concentration on Reaction Rate

If the temperature of the system is maintained constant, then the rate of reaction is determined by the concentrations of the substances making up the system. In the first place, one should speak of the concentrations of the reactants in a given reaction. However, the concentrations of the reaction products often has a bearing on the rate as well: if they accelerate the reaction, the term **autocatalysis** is used, and if the products slow down the reaction, the use of the term **autoinhibition** is justified. If the reaction rate is influenced by a substance (or a body) which is present in the system in an unchanged amount and which is not a direct participant in the reaction, then such a substance or body is called a **catalyst**.

A mathematical formula that relates the reaction rate to the concentrations is termed the rate equation or the kinetic equation. It is very important to note that in a general case the form of the kinetic equation cannot be predicted on the basis of the stoichiometric equation of the reaction. Thus, the reactions of hydrogen with iodine and bromine vapours are expressed by means of the same stoichiometric equations, but the kinetic equations used for them are quite different:

for H<sub>2</sub> + I<sub>2</sub> = 2HI 
$$\frac{dc_{HI}}{dt} = kc_{H_2}c_{I_2}$$
  
for H<sub>2</sub> + Br<sub>2</sub> = 2HBr  $\frac{dc_{HBr}}{dt} = \frac{kc_{H_2}c_{Br_2}^{1/2}}{1 + k'\frac{c_{HBr}}{c_{Br_2}}}$ 

The difference in the rate equations is accounted for by the difference in the reaction mechanisms.

The basic law of kinetics (the Law of Mass Action) follows from a large body of experimental data and expresses the dependence of the reaction rate on concentration:

The rate of any reaction is at each instant proportional to the product of the concentrations of the reactants, with each concentration raised to a power equal to the number of molecules of each species participating in the process.

If the empirical equation of the reaction is written in the following form:

$$v_1A + v_2B + v_3D \longrightarrow products$$

then the mathematical formulation of the basic law may be presented in the form:

$$w = -\frac{dc_{A}}{dt} = kc_{A}^{p}c_{B}^{q}c_{D}^{r} \dots$$
 (1.8)

In this equation, the proportionality factor k is, as a matter of fact, independent of the concentrations; it is quite different for different reactions and is strongly dependent on temperature. The proportionality factor k is called the **rate constant**. The physical meaning of the rate constant can easily be found if we set  $c_A = c_B = c_D = 1$ . Then

$$w = k$$

that is, k is numerically equal to the reaction rate at concentrations of the reactants equal to unity. In this connection, k is also called the **specific rate** (or *specific velocity*) of reaction. For reactions that obey equations of this type, the concept of **kinetic order** or simply **order of reaction**, n, may be introduced. By -definition

$$n = p + q + r + \dots$$

that is, by the order of a chemical reaction is meant the sum of all the exponents to which the concentrations in the rate equation are raised. In studying kinetics, reactions are usually classified according to the order of reaction. The following cases are the simplest ones:

(1) 
$$n = 0 - \frac{dc}{dt} = k_0$$
 zero order

(2) 
$$n = 1 - \frac{dc}{dt} = k_1 c$$
 first order

(3) 
$$n = 2 - \frac{dc}{dt} = k_{11}c^2$$

$$= k_{11}c_1c_2$$
second order

(4) 
$$n = 3 - \frac{dc}{dt} = k_{111}c^3$$
  
=  $k_{111}c_1^2c_2$   
=  $k_{111}c_1c_2c_3$  third order

The overall kinetic order higher than the third order is not practically encountered. Any exponent taken separately is called the reaction order with respect to a given substance.

Sometimes, the conditions under which a reaction is taking place are such that the concentration of one reactant or the concentrations of two or more reactants remain constant or nearly constant. Then the corresponding concentration factors can be lumped into a constant and the apparent reaction order decreases. In such cases, we speak of a reaction of the pseudo *n*th order, where *n* is now the sum of the exponents to which the variable concentrations are raised. Typical examples are catalytic reactions in which the concentration of the catalyst is constant; reactions in buffer solutions in which the hydrogen ion concentration is kept nearly constant; and also cases where one reacting substance is present in a large excess.

As an example may be cited the reaction of inversion of cane sugar (saccharose or sucrose):

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{H^+} 2C_6H_{12}O_6$$

which is speeded up by strong acids (hydrogen ions). The rate equation for this reaction

$$-\frac{dc_{\text{sug}}}{dt} = kc_{\text{sug}}c_{\text{H}_2\text{O}}c_{\text{H}^+}$$

indicates that the reaction is third order. But the concentration of the catalyst, hydrogen ions, does not alter during the course of the reaction, and the concentration of water in aqueous solution is high as compared with the concentrations of the other substances. Only the concentration of the sugar varies, i.e., the reaction is found to be pseudo-first order.

The exponents  $p, q, r \dots$  are usually positive integers, but there are cases where they may be fractional and even negative. The appearance of such complications is accounted for by a more or less complicated mechanism of the reaction.

In the old literature, and sometimes in the current literature, first-order, second-order and third-order reactions are called, respectively, unimolecular, bimolecular, and termolecular reactions. But these terms must not be confused since the second series of terms characterize the **molecularity** of a reaction—the number of molecules that participate in an elementary reaction step. Molecularity is thus a theoretical quantity which is introduced after a detailed study of kinetics when there is ground for judging about the reaction mechanism. The numerical value of molecularity assigned to a given reaction may vary with the appearance of more precise experimental data. A certain difficulty in distin-

guishing between the purely empirical quantity, order of reaction, and the molecularity probably consists in that unimolecular, bimolecular and termolecular reactions are at the same time first-order, second-order and third-order reactions, as will be shown at a later time, but the inverse conclusion may prove quite erroneous.

In general, the theoretical concept of molecularity may be used only in the case of simple elementary reactions, i.e., when there is sufficient ground for regarding the reaction as proceeding in a single elementary act. Such elementary reactions include, for example, the decomposition of azomethane:

$$CH_3N : NCH_3 \longrightarrow C_2H_6 + N_2$$

The elementary act involves one molecule—the reaction is unimolecular. If two molecules are involved in a single act

$$Cl + H_2 \longrightarrow HCl + H$$
  
 $H_2 + I_2 \longrightarrow 2III$ 

then such reactions are called bimolecular reactions. Accordingly, in a termolecular reaction, three particles (molecules) participate in one elementary act. For example, the reaction of recombination of atoms into molecules is termolecular:

$$H + H + M \longrightarrow H_2 + M$$

Here M, a third particle, may be, in a particular case, a hydrogen molecule or any other particle. As will be shown at a later time, it is precisely in the case of such elementary reactions that the numerical values of molecularity and kinetic order of reaction coincide. Thus, the reaction

$$H + H + H_2 \longrightarrow H_2 + H_2$$

is a termolecular and third-order reaction simultaneously.

The majority of reactions that the chemist has to deal with are however not simple, though sometimes they might seem to be simple. For instance, the thermal decomposition of dichloroethane vapour

$$CH_2CI-CH_2CI \longrightarrow CHCI=CH_2 + HCI$$

leading to the formation of vinyl chloride and hydrogen chloride may be thought, by analysis, to be a simple reaction. A preliminary study of the kinetics of the reaction points to first order, i.e., the kinetic equation has the form:

$$-\frac{dc}{dt} = k_1 c$$

where c is the concentration of dichloroethane. But this reaction however cannot be called unimolecular since a more detailed

study of the kinetics shows that its mechanism is complicated. The reaction proceeds in several stages, including the formation of free atoms and radicals:

- (1)  $C_2H_4Cl_2 \longrightarrow C_2H_4Cl + Cl$
- (2)  $Cl + C_2H_4Cl_2 \longrightarrow C_2H_3Cl_2 + HCl$
- (3)  $C_2H_3Cl_2 \longrightarrow C_2H_3Cl + Cl$
- $(4) \quad C_2H_4C1 + C1 \longrightarrow C_2H_4C1_2$

The first and third steps in this mechanism are unimolecular, and the second and fourth steps are bimolecular. Evidently, we cannot speak of the molecularity of the decomposition of dichloroethane as a whole. At the same time, we may speak of its experimental kinetic first order.

## Application of the Basic Law of Kinetics to Simple Reactions

#### 2.1. First-Order Reactions

If we write the equation for a generalized chemical reaction, we shall assume that only one substance A \* enters into a first-order reaction:

$$v_1A \longrightarrow v_1'E + v_2'B$$

We shall express the concentration of the substance A in moles per litre. Let the concentration of A be equal to a at the start of the reaction (t = 0); after the lapse of time t it decreases to a - x. Hence, x expresses the decrease of the concentration. The rate constant is denoted by the symbol  $k_{\rm I}$ . Then at time t the rate will be equal to

$$-\frac{d(a-x)}{dt} = \frac{dx}{dt} = k_{\mathrm{I}}(a-x) \tag{2.1}$$

Now we separate the variables and integrate between limits from 0 to t and from 0 to x:

$$\int_{0}^{x} \frac{dx}{a - x} = k_{\rm I} \int_{0}^{t} dt \tag{2.2}$$

We obtain

$$\ln \frac{a}{a-x} = k_1 t \tag{2.3}$$

OL

$$k_{\rm I} = \frac{2.303}{t} \log \frac{a}{a - x} \tag{2.4}$$

Using the integrated formula (2.4), we can check up whether the reaction under consideration is first order. For this to be done, we determine experimentally the decrease in the concentration at different times:

$$t = 0,$$
  $t_1, t_2, t_3, ...$   
 $x = 0,$   $x_1, x_2, x_3, ...$ 

<sup>\*</sup> As pointed out above, this is not necessarily the case if the concentrations of the other participants remain constant.

and, using Equation (2.4), we calculate the values of  $k_1$  for various times t. If we obtain identical values of  $k_1$  within the experimental error, then the quantity  $k_1$  may be considered a constant and the reaction under study, a first-order reaction. But if  $k_1$  does not remain constant, other assumptions should be made concerning the order of the reaction.

The integrated formula (2.4) is often written in a different

form:

$$a - x = ae^{-k} \mathbf{I}^{\mathsf{t}} \tag{2.5}$$

or

$$a = a \left( 1 - e^{-k_{\parallel} t} \right) \tag{2.6}$$

In this connection, mention is often made of the exponential dependence of the concentration of the reacting substance on time. These relationships were derived for the first time in 1850 by Wilhelmy, who measured the rate of conversion of an acidic solution of sucrose into glucose and fructose before the formulation of the basic law of kinetics (the Law of Mass Action) by C. M. Guldberg and P. Waage (1864).

Certain conclusions must be made at this point. First, from the formulas obtained it follows that the dimensions of the first-order rate constant correspond to the reciprocal time  $(t^{-1})$  and it may

be expressed in reciprocal seconds, minutes, hours, etc.

Second, since the concentrations are included in the formulas, say, (2.4), in the form of a ratio, evidently it is immaterial in what units they are expressed: the value of the rate constant will not change. It also follows from the dimensions of  $k_1$ —it does not contain the concentration. Instead of the concentration, use may be made of the total number of molecules N. Then Equations (2.4) and (2.5) will assume the following forms, respectively:

$$\ln \frac{N_0}{N} = k_1 t \tag{2.7}$$

and

$$N = N_0 e^{-k_{\parallel} t} \tag{2.8}$$

Further, it is important that in first-order reactions to identical time intervals there correspond identical fractions of the substance that has reacted.\* The term half-life period (or simply half-life) is most often introduced, i.e., the time required for one-half of the reactant to undergo reaction or the time taken for 50% reaction to occur. Counting the time from the start of the reaction, we assume that x = (1/2)a. Then, according to Equation (2.4), we get the following relation:

$$\ln 2 = k_1 (T_{1/2})_1$$
 or  $(T_{1/2})_1 = \frac{\ln 2}{k_1} = \frac{0.643}{k_1}$  (2.9)

<sup>\*</sup> Relation (2.5) derived by L. Wilhelmy was based on this proposition.

which allows us to find the half-life  $(T_{\frac{1}{2}})_1$  of a first-order reaction. As seen from the formula, it is determined exclusively by the rate constant.

Figure 2.1 shows the change of the amount (or concentration) of the substance which reacts by first order. Here the time is expressed in units of the half-life period.

As can be seen from the formulas obtained and from Fig. 2.1, the substance reacts completely only for an infinitely large period of time.

Now we introduce another, very important concept, the average lifetime,  $\tau$ , of the molecules of a substance which reacts by first-

order kinetics. At time t when N molecules are present in the system, the rate of the reaction is equal to

or 
$$-\frac{dN}{dt} = k_{I}N$$

$$-dN = k_{I}N dt$$
 (2.10)

Obviously, -dN is the decrease in the number of molecules for the time period from t to t+dt and dN is equal to the number of molecules that have survived up to time t and decomposed during the subsequent infi-

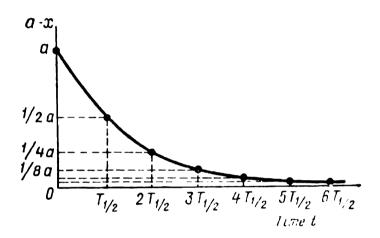


Fig. 2.1. The course of a first-order reaction — formula (2.5).

The time t is expressed in units of the half-life  $T_{1/2}$ . The difference (a-x) is the concentration of the reactant.

nitely short time period dt. Multiplying — dN by t, we find the total lifetime of these molecules. If we replace simultaneously N on the right-hand side of the equation by its value from Equation (2.8), we will obtain:

$$-t \, dN = k_I N_0 t e^{-k_1 t} \, dt \tag{2.11}$$

All the molecules will react for an infinitely large time period, and therefore the total lifetime of all the molecules taken initially can be found by integrating the right-hand side of expression (2.11) from 0 to  $\infty$ . Dividing the integral by the total number of molecules, we shall finally determine the average lifetime:

$$\tau = \frac{k_1 N_0 \int_0^\infty t e^{-k_1 t} dt}{N_0} = k_1 \int_0^\infty t e^{-k_1 t} dt$$
 (2.12)

Now we integrate by parts and obtain:

$$\tau = \frac{1}{k_{\rm I}} \tag{2.13}$$

Thus, the average lifetime is equal to the reciprocal value of the rate constant. Relation (2.13) is very important since it allows us to get a deeper insight into the physical significance of the rate constant of a first-order reaction. At a later time (see Chapter 8), the relation between  $\tau$  and  $k_{\rm I}$  will be used in expounding one of the theories of chemical kinetics.

Let us now consider some examples of first-order reactions. One example is the thermal decomposition of gaseous acetone at

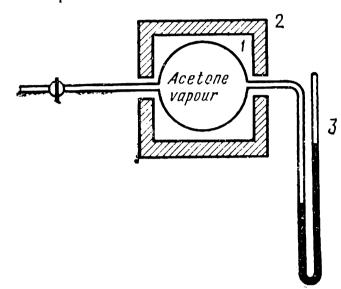


Fig. 2.2. Apparatus for conductin the decomposition of acetone:

1 — reaction vessel; 2—furnace; 3 — manometer.

504°C. According to analysis, acetone decomposes in the following manner:

$$CH_2COCH_3 (gas) \longrightarrow C_2H_4 + CO + H_2$$

The kinetics of the reaction is studied by the manometric method, i.e., the course of the reaction is followed by measuring the pressure in a closed vessel (Fig. 2.2, Table 2.1).

The pressure values in the reaction vessel given in Table 2.1 are measured by means of a pressure gauge at times indicated in the first column of

the table. From Table 2.1 it is seen that during the course of the reaction the pressure increases almost by three times. This corresponds to the stoichiometric equation given above. The ratio of the numbers of moles of acetone in the system are calculated from the formula

$$\frac{N_0}{N} = \frac{2P_0}{3P_0 - P}$$

which is easily derived on the basis of the Avogadro law.

The rate constants calculated on the assumption of first order exhibit satisfactory constancy. Therefore, the assumption of first order may be considered to have been confirmed. From the average rate constant there are determined other kinetic characteristics of the reaction, namely, the average lifetime of acetone molecules at 504 °C:

$$\tau = \frac{1}{k_1} = 2344 \sec \approx 39 \, \text{min}$$

and also the half-life period:

$$(T_{1/2})_1 = 0.693\tau = 1580 \text{ sec} = 26 \text{ min } 20 \text{ sec}$$

True unimolecular or, better, monatomic, mononuclear first-order processes include all the numerous transformations of radioactive

Time from start of experiment, sec	Pressure in reaction vessel, min Hg	$\frac{N_0}{N}$	$k_{1} = \frac{2.303}{t} \log \frac{N_{0}}{N},$ $\sec^{-1} \times 10^{4}$
0	312	1	
390	408	1.181	4.26
<b>7</b> 77	488	1.392	4.27
1195	562	1.666	4.26
. 3155	779	3.960	4.30
	931		

TABLE 2.1. Kinetics of the Thermal Decomposition of Acetone at 504°C

The average value of  $k_1 = 4.27 \times 10^{-4} \text{ sec}^{-1}$ .

substances. These processes are known to be studied by a special branch of chemistry—radiochemistry; they differ from ordinary chemical reactions by their rate being independent of temperature and other effects used in the chemical laboratory. Thus, for example, radon undergoes  $\alpha$ -decay, forming the so-called radium A, one of the isotopes of the Group VI element polonium:

$$Rn_{86}^{222} \longrightarrow \alpha_2^4 + RaA_{82}^{218}$$

The rate of the process is characterized by the following values of the constants:  $k_1 = 2.1 \times 10^{-6} \text{ sec}^{-1}$ ;  $\tau = 5.5 \text{ days}$ ,  $T_{1/2} = 3.8 \text{ days}$ . Other radioactive substances disintegrate at velocities differing

by many orders of magnitude. Some data are given in Table 2.2.

TABLE 2.2. The Kinetic Characteristics of the Decay of Some

Radioactive Substances

Substance	$k_1$ , sec <sup>-1</sup>	$T_{1/2}$
Uranium	$1.37\times10^{-11}$	4.5×10° years 1590 years 1.5×10 <sup>-4</sup> sec

Certain physical processes are also described by first-order equations. One example is the spontaneous radiation of electronically excited atoms and molecules. Some pertinent data are presented in Chapter 10 (Table 10.3) in connection with the discussion of the kinetics of photochemical reactions.

In general, the electronically excited states of atoms and molecules have quite different average lifetimes. States with relatively

large  $\tau$  values, of the order of  $10^{-3}$  to  $10^{-4}$  sec, are called metastable.

A classical example of first-order reactions is the reaction of inversion of cane sugar (a biose) which is decomposed in aqueous solution in the presence of acids into two isomeric monoses—fructose and glucose:

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{H_3O^+} 2C_6H_{12}O_6$$

The rate equation for this reaction is known to be the following:

$$-\frac{dc_{\text{sug}}}{dt} = k_1 c_{\text{sug}}$$

where  $c_{\text{sug}}$  is the concentration of cane sugar (sucrose). Evidently, this equation is first order since, though the reaction also involves water and hydrogen ions, their concentrations remain unchanged ( $H_3O^+$  ions serve as the catalyst and water is present in a very large excess). Both these constant concentrations may be regarded as being incorporated into the constant  $k_1$ .

The inversion of sucrose is convenient for studying kinetics since, first, it proceeds at temperatures close to room temperature and, second, in the course of this reaction the angle of rotation of the plane of polarization is changed. Sucrose rotates the plane of polarization to the right, and the mixtures of monoses to the left. A solution of sucrose is placed in a polarimeter tube and the course of the reaction can be followed without interrupting the reaction. The concentrations are calculated by using the proportional relation between the angle of rotation and the concentration of the rotating substance.

The hydrolysis of esters, say, ethyl acetate, in aqueous solution in the presence of strong acids

$$CH_3COOC_2H_5 + H_2O \xrightarrow{H_3O^+} CH_3COOH + C_2H_5OH$$

is also characterized by first-order kinetics. Since one of the products is an acid, the course of the reaction can be conveniently followed by taking samples of the solution and titrating them with alkali.

Some interesting specific features (to be discussed at a later time) are displayed by another first-order reaction—the decomposition of nitrogen pentoxide in the gas phase:

$$N_2O_5 \longrightarrow N_2O_4 + \frac{1}{2}O_2$$

This reaction proceeds at the same velocities in various solvents as well.

#### 2.2. Second-Order Reactions

Second-order reactions are rather numerous. Such are, for example, the reactions of formation and decomposition of hydrogen iodide:

$$H_2 + I_2 \text{ (vapour)} \longrightarrow 2III$$
 (I)

$$2HI \longrightarrow H_2 + I_2 \text{ (vapour)} \tag{II)}$$

These reactions have been thoroughly studied and the theory of active collisions, which is one of the theories of chemical kinetics, was first applied to these reactions.

Examples of second-order reactions are a number of hydrolytic reactions in alkaline solutions, in particular, the saponification of ethyl acetate in aqueous solution:

$$CH_3COOC_2H_5 + NaOH \longrightarrow CH_3COON_3 + C_9H_5OH$$
 (III)

The decomposition of nitrogen dioxide

$$2NO_2 \longrightarrow 2NO + O_2$$

and usually the reactions of dimerization proceed as second-order reactions; an example is the dimerization of cyclopentadiene:

e is the dimerization

$$\begin{array}{ccc}
CH_2 \\
2HC \nearrow CH \\
\parallel & \parallel \longrightarrow & C_{10}H_{12} \\
C \longrightarrow & C \\
\parallel & \parallel & H
\end{array}$$
ioned above are ordin

The reactions mentioned above are ordinary chemical reactions; these reactions can be followed directly by using relatively simple methods of chemical analysis. Second-order reactions, however, include numerous bimolecular reactions involving atoms and free radicals. A study of the rates of such reactions presents an incomparably more formidable experimental task and is one of the latest achievements. As examples may be cited some reactions with the participation of free hydrogen and oxygen atoms:

$$H + Br_2 \longrightarrow HBr + Br$$
 $H + HBr \longrightarrow H_2 + Br$ 
 $H + H_2 (para) \longrightarrow H_2 (ortho) + H$ 
 $O + H_2 \longrightarrow OH + H$ 

These are so-called elementary reactions which make up, in many cases, the "mechanisms" of complex chemical transformations. They will be discussed later in the text.

Let us now consider second-order reactions from the standpoint of the basic law of kinetics. We shall first examine a simple case where either one single substance reacts by second-order kinetics.

reaction (II), or two substances entering into reaction in equivalent amounts, reaction (I), are present at equal concentrations. In these cases the rate is determined by one concentration. If we denote the reaction rate as a - x, where a is the initial concentration, we obtain a differential rate equation:

$$-\frac{d(a-x)}{dt} = \frac{dx}{dt} = k_{II}(a-x)^2$$
 (2.14)

Here  $k_{II}$  is the second-order rate constant. Separating the variables and integrating, we obtain:

$$\frac{1}{a-x} - \frac{1}{a} = k_{11}t \tag{2.15}$$

or

$$\frac{x}{a\left(a-x\right)} = k_{\text{II}}t\tag{2.16}$$

and also

$$x = \frac{a^2 k_{II} t}{1 + a k_{II} t} \tag{2.17}$$

These are formulas that express, for second-order reactions, the dependence of the concentration of the reacting substance on time.

Certain conclusions should be made at this point. From relations (2.15) through (2.17) it follows that the dimensions of the second-order rate constant are more complex than those of the first-order constant:

$$[k_{11}] = [c^{-1}t^{-1}] (2.18)$$

that is, apart from time, it also includes the reciprocal concentration. If the concentration is expressed in moles per litre, then

$$[k_{11}] = [\text{litre} \cdot \text{mole}^{-1} \cdot \text{time}^{-1}]$$

Thus, the numerical value of the rate constant depends on the choice of concentration units also.

The application of the concept of the half-life, which is quite clear for first-order reactions, is somewhat complicated in reactions of higher orders. The simplest examples are those in which one substance reacts by second-order kinetics or two substances are present at equal concentrations. For more complicated conditions we may use the concept of half-life (half-conversion) period with respect to any one substance.

Let us consider the simplest case. Substituting the value of  $x = \frac{1}{2}a$  into formula (2.15), we obtain:

$$(T_{1/2})_{11} = \frac{1}{ak_{11}} \tag{2.19}$$

Hence, for second-order reactions the half-life depends not only on the rate constant; it is also inversely proportional to the first power of the initial concentration. The dependence of  $T_{1/2}$  on a forms the basis of one of the methods of determining the reaction order.

Let us examine how to calculate the kinetics of a second-order reaction, using as an example the saponification of ethyl acetate with alkali in aqueous solution [reaction (III)] at 20.5 °C. In a vessel placed in a thermostat, the ethyl acetate and alkali solutions that have been kept in the thermostat are mixed so that the concentrations of the substances in the mixture are equal. For example,

$$a = c_{\rm ester} = c_{\rm alkali} = 0.02$$
 mole/litre

The moment of mixing is regarded as the beginning of the reaction and the time zero. Then, at certain intervals, samples are taken and subjected to titration with acid, the concentration of the alkali left (and of the ester) being determined. The results are presented in Table 2.3.

TABLE 2.3. The Kinetics of the Saponification of Ethyl Acetate with Alkali at 20.5 °C

Time when sample is taken t, sec	$c_{\text{ester}} = c_{\text{alkali}} = a - x$ , mole/litre $\times 10^2$	$k_{II} = \frac{1}{t} \frac{a}{a (a-x)},$ $litre \cdot mole^{-1} \cdot sec^{-1}$	$k_{\mathrm{I}} = \frac{2.3}{t} \log \frac{a}{a - x},$ $\sec^{-1} \times 10^{4}$
0	2.00	_	_
300	1.280	0.094	14.9
1380	0.540	0.090	9.3
3300	0.289	0.090	5.8
7200	0.138	0.095	3.7

The average value of  $k_1$  is  $4.27 \times 10^{-4}$  sec<sup>-1</sup>.

The values of  $k_{II}$  given in Table 2.3 have been calculated by formula (2.16). As seen,  $k_{II}$  exhibits quite satisfactory constancy: the observed variations do not exceed the limits of the experimental error and the main point is that there is no systematic variation of the constant or, as is often said, of its course. The second order may then be considered to have been confirmed. The values of the first-order rate constant,  $k_{I}$ , are given for comparison. As can be seen,  $k_{I}$  decreases systematically as the reaction proceeds. This is of course quite understandable since instead of the second-order equation

$$\frac{dx}{dt} = k_{\text{II}} (a - x)^2 \tag{2.20}$$

we used the first-order equation:

$$\frac{dx}{dt} = [k_{II} (a - x)] (a - x) = k_{I} (a - x)$$
 (2.21)

that is, the decreasing concentration of the reactant is found to have been incorporated into the quantity  $k_{\rm f}$ .

Generally, the systematic decrease of the rate constant is a sign of the underestimation of the supposed order and vice versa.

Let us consider the application of the basic law of kinetics to a second-order reaction written in the most general form:

$$v_1A + v_2B \longrightarrow products$$

The differential equation for the reaction rate has the following form in this particular case:

$$w = -\frac{dc_{A}}{dt} = k_{II}c_{A}c_{B} \tag{2.22}$$

Further, for the integration to be carried out, it is necessary to establish the relation between the concentrations  $c_A$  and  $c_B$ . If we let a and b be the initial concentrations of A and B, respectively, and  $c_B$  the decrease in concentration of  $C_B$  by time  $C_B$  then  $C_A$  and  $C_B$  and  $C_B$  becomes

$$w = -\frac{dc_{A}}{dt} = \frac{dx}{dt} = k_{II} (a - x) \left( b - \frac{v_{2}}{v_{1}} x \right)$$
 (2.23)

Separating the variables, we obtain:

$$\frac{dx}{(a-x)\left(b-\frac{v_2}{v_1}x\right)} = k_{11} dt$$
 (2.24)

For integration to be performed, we decompose the fraction on the left-hand side of Equation (2.24) into partial fractions, using the coefficients  $\varphi_1$  and  $\varphi_2$  to be determined:

$$\frac{1}{(a-x)\left(b-\frac{v_2}{v_1}x\right)} = \frac{\varphi_1}{a-x} + \frac{\varphi_2}{b-\frac{v_2}{v_1}x} = \frac{\varphi_1\left(b-\frac{v_2}{v_1}x\right) + \varphi_2(a-x)}{(a-x)\left(b-\frac{v_2}{v_1}x\right)}$$

It is obvious that the numerator of the last fraction is identical with unity:

$$\varphi_1\left(h - \frac{v_2}{v_1}x\right) + \varphi_2(a - x) \equiv 1$$
 (2.25)

Since equality (2.25) must be satisfied at any value of x, we determine the coefficients  $\varphi_1$  and  $\varphi_2$  by substituting into equality

(2.25) the quantities  $(v_1/v_2)b$  and a separately instead of x. Thus,

$$\varphi_1 = \frac{1}{b - \frac{v_2}{v_1} a} \quad \text{and} \quad \varphi_2 = \frac{1}{a - \frac{v_1}{v_2} b}$$

Hence,

$$\int \frac{dx}{(a-x)\left(b-\frac{v_2}{v_1}x\right)} =$$

$$= \int \left(\frac{1}{b-\frac{v_2}{v_1}a} \cdot \frac{1}{a-x} + \frac{1}{a-\frac{v_1}{v_2}b} \cdot \frac{1}{b-\frac{v_2}{v_1}x}\right) dx =$$

$$= k_{II}t + \text{const} = -\frac{1}{b-\frac{v_2}{v_1}a} \ln (a-x) - \frac{\frac{v_1}{v_2}}{a-\frac{v_1}{v_2}b} \ln \left(b-\frac{v_2}{v_1}x\right) =$$

$$= \frac{v_1}{v_2a-v_1b} \ln \frac{a-x}{b-\frac{v_2}{v_1}x}$$

The integration constant is found from the initial condition x = 0 at t = 0, i.e.,

$$const = \frac{v_1}{v_2 a - v_1 b} \ln \frac{a}{b}$$

Finally we arrive at the integrated formula for the general case of a second-order reaction:

$$\frac{v_1}{v_2 a - v_1 b} \ln \frac{b (a - x)}{a \left(b - \frac{v_2}{v_1} x\right)} = k_{11} t \tag{2.26}$$

A simpler and frequently encountered variant of this formula is obtained if the stoichiometric coefficients are equal, i.e.,  $v_1 = v_2$ :

$$\frac{1}{a-b} \ln \frac{b (a-x)}{a (b-x)} = k_{11}t \tag{2.27}$$

The dimensions of  $k_{II}$  in expressions (2.26) and (2.27) are of course the same as in a simpler case, i.e.,  $[c^{-1}t^{-1}]$ .

The concept of the half-life period (better, the half-conversion period) may be employed in these cases only with respect to one of the reacting substances. Thus, substituting x = (1/2)a into Equation (2.26), we get

$$T_{1/2}(\Lambda) = \frac{v_1}{k_{11} (v_2 a - v_1 b)} \ln \frac{v_1 b}{2v_1 b - v_2 a}$$
 (2.28)

the half-life for substance A, which depends on both initial concentrations.

It should be noted that Equations (2.26) and (2.27) are inapplicable with the stoichiometric ratio of the initial concentrations, i.e., when  $a/b = v_1/v_2$ ; as can easily be seen, in this case the equations turn into indeterminate forms which must be evaluated. Considering Equation (2.27) as the ratio of two functions, we replace it by the ratio of the derivatives of b at constant a and x:

$$\frac{a (b - x)}{b (a - x)} \cdot \frac{a (b - x) (a - x) - b (a - x) a}{a^{2} (b - x)^{2}}$$

Passing over to the limit  $b \rightarrow a$ , we obtain, as should be expected, the following relation:

$$\frac{1}{a-x} - \frac{1}{a} = k_{11}t$$

which has been found earlier for the simplest dependence of the rate on the square of one concentration.

Let us consider formula (2.27) from another aspect. Suppose that the initial concentration of one of the reactants is much higher than the concentration of the other, say  $b \gg a$ . Then the small values of a and x may be neglected as compared to b. Thus, we obtain the equation:

$$\ln \frac{a}{a-x} = [k_{11}b] = k_1t \tag{2.29}$$

in which the large (and practically constant) concentration b is incorporated into the constant  $k_1$ . It is obvious that Equation (2.29) formally coincides completely with the first-order equation considered earlier. Such pseudo-first-order reactions are encountered rather frequently. Especially typical are reactions where the second reagent is a solvent. In this category are included the above-mentioned hydrolysis of ethyl acetate in aqueous solution in the presence of acid and the inversion of sucrose.

#### 2.3. Third-Order Reactions

We shall consider third-order reactions from the viewpoint of the basic law of kinetics. From the mathematical standpoint, the simplest case is one where three substances that react in equivalent amounts are all present initially at equal concentrations in the system:

$$A + B + C \longrightarrow products$$

The initial concentrations  $c_A = c_B = c_C = a$ , and the concentrations at any time are equal to a - x. The rate of the reaction will be written thus:

$$w = \frac{dx}{dt} = k_{III} (a - x)^3$$
 (2.30)

Integrating gives the following formula:

$$\frac{1}{2} \left\{ \frac{1}{(a-x)^2} - \frac{1}{a^2} \right\} = k_{111}t \tag{2.31}$$

which expresses the dependence of the concentration on time. The dimensions of the third-order rate constant are clear from the relations written above:

$$[k_{III}] = [c^{-2}t^{-1}] \tag{2.32}$$

In particular, if the concentration is expressed in moles per litre, we obtain the dimensions (litre<sup>2</sup>·mole<sup>-2</sup>·time<sup>-1</sup>). Thus, the numerical value of  $k_{III}$  is, to an even larger extent than  $k_{II}$ , dependent on the choice of concentration units.

If we continue using the term half-life period, then x = (1/2)a should be substituted into Equation (2.31):

$$\frac{1}{2} \left\{ \frac{4}{a^2} - \frac{1}{a^2} \right\} = k_{III} (T_{1/2})_{III}$$

Thus, the half-life is given by

$$(T_{1/2}) = \frac{3}{2a^2k_{III}} \tag{2.33}$$

Since reactions of higher order than the third are practically not encountered, we may at this point sum up the dependence of  $T_{1/2}$  on the initial concentration. This is done in Table 2.4 which also contains *n*-order reactions.

TABLE 2.4. The Dimensions of the Rate Constants and the Half-Life Periods for Reactions of Various Orders

Reaction order	Dimensions of the rate constant	T <sub>1</sub> / <sub>2</sub>
1 2 3 n	$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	$\begin{vmatrix} \ln 2/k_{\rm I} \\ 1/c_0k_{\rm II} \\ 3/2c_0k_{\rm III} \\ (2^{n-1}-1)/(n-1)c_0^{n-1}k_n \end{vmatrix}$

It will be recalled that for reactions of higher order than the first, expressions for  $T_{1/2}$  are of limited importance. They are derived for a case where the substances reacting in equivalent amounts are initially present at equal concentrations.

Let us consider some examples of third-order reactions. There are a few such reactions among ordinary gas reactions and almost all of them involve nitric oxide. They include an important industrial reaction of oxidation of nitric oxide with oxygen, one of

the stages of preparation of nitric acid:

$$2NO + O_2 \longrightarrow 2NO_2$$

This reaction is second order in NO and first order in O2:

$$\frac{dc_{\text{NO}_2}}{dt} = k_{\text{III}} c_{\text{NO}}^2 c_{\text{O}_2} \tag{2.34}$$

We shall examine this reaction in more detail in connection with its anomalous dependence on the rate and temperature. Whereas for the vast majority of reactions the rate constants increase with rise of temperature \*,  $k_{111}$  for the oxidation of nitric oxide decreases, as can be seen from Table 2.5.

TABLE 2.5. The Dependence of the Rate Constant of the Oxidation of Nitric Oxide on Temperature

t, °C	$k_{\text{III}}$ , litre <sup>2</sup> ·mole <sup>-2</sup> ·sec <sup>-1</sup> ·10 <sup>-3</sup>	t, °C	$k_{\text{III}}$ , litre <sup>2</sup> ·mole <sup>-2</sup> ·sec <sup>-1</sup> ·10 <sup>-3</sup>
45	10.1	140	4.0
+27	7.1	291	2.8

One of the explanations for the anomaly in question consists in assuming that this reaction proceeds in two consecutive steps:

I. 
$$2NO \longrightarrow N_2O_2$$
 fast  
II.  $N_2O_2 + O_2 \longrightarrow 2NO_2$  slow

The first step is a fast, reversible and exothermic reaction. The concentration of the dimer  $N_2O_2$  corresponds to the thermal equilibrium and it can be determined by means of the equilibrium constant:

$$K_c = \frac{c_{\rm N_2O_2}}{c_{\rm NO}^2} \tag{2.35}$$

The slow consumption of the dimer at the second stage does not practically alter its equilibrium concentration. But since reaction I is exothermic, the equilibrium constant and, hence, the concentration of the dimer, falls off with temperature.

For the observed reaction rate to be calculated, it is necessary to introduce an important and sufficiently self-evident rule stating that the overall rate of any process consisting of a number of consecutive steps is determined by the rate of the slowest step. In this particular case, the slow step is the second step. Hence, the

<sup>\*</sup> The dependence k = f(T) will be considered in detail in Chapter 4.

observed rate will be expressed by the equation

$$\frac{dc_{\text{NO}_2}}{dt} = k_{\text{II}} c_{\text{N}_2\text{O}_2} c_{\text{O}_2}$$

in which the concentration of the dimer may be replaced by using relation (2.35):

$$\frac{dc_{\text{NO}_2}}{dt} = k_{11}K_c c_{\text{NO}}^2 c_{\text{O}_2} = k_{111}c_{\text{NO}}^2 c_{\text{O}_2}$$
 (2.36)

In the last equation the product  $k_{II}K_c$  is designated by  $k_{III}$ . Expression (2.36) functionally coincides completely with the experimentally found kinetic equation (2.34). It now remains to assume only that the decrease of  $K_c$ , i.e., the equilibrium constant of an exothermic reaction, with temperature covers the possible increase of  $k_{II}$  and this leads to a decrease of their product, i.e.,  $k_{III}$ . Such is one of the possible explanations for the decrease of the rate constant for the oxidation of nitric oxide with rise of temperature.

Third-order reactions include also the reactions of formation of nitrosyl chloride and bromide, which are similar to the previous reaction:

$$2NO + Cl_2 \longrightarrow 2NOCI$$

and

$$2NO + Br_2 \longrightarrow 2NOEr$$

There are more third-order reactions in solutions than in gases. We shall limit ourselves to only one example, the reduction of ferric chloride with stannous chloride:

$$2FeCl_3 + SnCl_2 \longrightarrow 2FeCl_2 + SnCl_1$$

Of special interest are numerous termolecular processes of recombination of atoms and simple radicals into molecules, which are also third-order reactions. The point is that reactions of the type

$$H + H \longrightarrow H_2$$

do not practically take place upon collision of two atoms, i.e., by a bimolecular mechanism. To illustrate, we shall consider the dependence of the potential energy of a diatomic molecule on the distance between the atoms, which is expressed by a curve obtained experimentally from spectroscopic data (Fig. 2.3). Curves of this type are approximately described by the Morse empirical equation:

$$U = D_e \left[ 1 - e^{-a (r - r_e)} \right]^2 \tag{2.37}$$

where  $D_e$  is the dissociation energy counted off from the minimum of the curve; a is a constant; r is the interatomic distance in the

molecule, and  $r_e$  is the distance corresponding to the minimum of potential energy.

At this point and hereafter it is useful to draw a certain mechanical analogy: the interconversions of kinetic and potential energies in a vibrating molecule may be visualized as the conversion of the energy of an imaginary heavy particle sliding in a gravitational field without friction along the trough simulating the profile of the potential energy curve. Thus, if the particle is

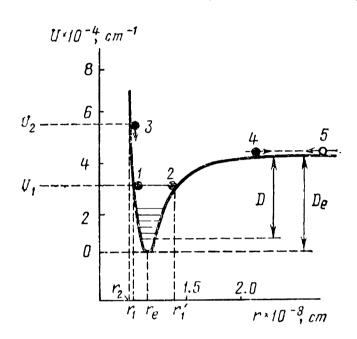


Fig. 2.3. The potential energy of a molecule versus the internuclear distance.

The quantities  $D_e$  and D are the "spectroscopic" and chemical energies of dissociation.

raised to height  $U_1$  (this corresponds to a decrease of the interatomic distance in molecule down to  $r_1$ ), then, while sliding down the curve, it will move at an ever increasing velocity. The greatest kinetic energy is assumed by the particle at the minimum point of the curve. This energy then be converted into the potential energy when the particle ascends the opposite portion of the curve up to the original height  $U_1$  (position 2). This is followed by the backward movement. It is clear that in the case under consideration particle will perform periodic motion from position I to position 2. This corresponds to

the periodic change of the interatomic distance in the molecule between  $r_1$  and  $r_1'$ , i.e., to the vibrating motion of atoms, which results from the initial compression of the molecule to  $r_1$ , say, upon collision with another molecule. But upon a stronger collision the molecule may be found to have been compressed to the distance  $r_2$ , i.e., the representative particle may be found to have been raised to the height  $U_2$ , which is greater than the limiting value  $D_e$ . In this case the particle, having passed the minimum, may move at some velocity along the right-hand horizontal branch to any distance. The motion will no longer be periodic. The molecule compressed to the distance  $r_2$  will split into two free atoms.

Now we shall examine the process of a bimolecular collision between two atoms. Suppose that a particle being in position 5 moves at a certain velocity to the side of decreasing r. Obviously, such a particle, having passed the minimum, will rise up the steep portion of the curve to a height greater than  $D_e$ , and in backward motion it will again come back to the horizontal portion

of the curve, corresponding to free, non-interacting atoms. Thus, upon a bimolecular collision the quasi-molecule formed has an energy greater than the dissociation limit  $D_e$  and therefore breaks down instantly.

In order to pass into a stable state with an energy lower than  $D_e$ , the quasi-molecule must evidently lose part of the energy of the relative motion of its atoms. How can this happen? First, the energy of the relative motion of the atoms in the molecule cannot turn, say, into the translational energy of motion of the molecule as a whole. This would violate the principle of conservation of momentum. Hence, this route to stabilization is excluded.

$$H + H \longrightarrow H_2 + hv$$

Theoretical calculations, however, show the low probability of the molecule being stabilized in this way, especially during the formation of molecules having no dipole moment (i.e., such as the  $H_2$  molecule).

Thus, the bimolecular formation of diatomic molecules does not practically occur. It is realized in a ternary collision, for example,

$$H + H + M \longrightarrow H_2 + M$$

where M is a third particle (a molecule or atom), the nature of which is not quite immaterial for the effectiveness of the given collision. The part played by the particle M is obvious — it carries away the excess energy that makes the molecule unstable. As shown by the kinetic theory of gases (see Chapter 6), the number of ternary collisions per unit volume per unit time is proportional to the product of the concentrations of the colliding particles. The rate of the reaction is also proportional to this product. As a matter of fact, as experiment shows, the rate with which the concentration of atoms diminishes is expressed by the equation:

$$-\frac{dc_{\mathrm{H}}}{dt} = k_{\mathrm{HI}}c_{\mathrm{H}}^2c_{\mathrm{M}} \tag{2.38}$$

that is, this reaction is a third-order reaction.

The recombination of other atoms and simple radicals occurs in an analogous manner \*:

$$O + O + M \longrightarrow O_2 + M$$
  
 $OH + OH + M \longrightarrow H_2O_2 + M$   
 $CH + CH + M \longrightarrow C_2H_2 - M$ 

and so on.

<sup>\*</sup> Further in the text the arrow above M, which indicates an energy increment for this particle, will be omitted.

It should however be noted that the more complex the radical, the greater is the probability of a bimolecular recombination; it is even significant for the  $CH_3$  radicals:

$$\begin{array}{ccc} H & H \\ H-C+C-H & \longrightarrow & C_2H_6 \\ H & & \end{array}$$

This is evidently explained by the fact that in complex molecules not only the atoms between which a bond is formed may vibrate but many other types of vibrating motion are also possible. It is for this reason that there appears the possibility of self-stabilization by way of energy redistribution within the molecule—its removal in this case from the C—C bond to the C—H bonds. The recombination of more complex radicals, say, ethyl radicals,

$$C_2H_5 + C_2H_5 \longrightarrow C_1H_{10}$$

is practically bimolecular.

In conclusion, let us consider the application of the basic kinetic law to a more complicated case of third-order reactions: three substances react in equivalent amounts but are present at different initial concentrations. If we write the reaction in a general form:

$$A + B + C \longrightarrow D + E + \dots$$

and denote the initial concentrations by a, b, and c, and the concentrations at various elapsed times by (a-x), (b-x), and (c-x), we shall obtain a differential rate equation:

$$\frac{dx}{dt} = k_{III} (a - x) (b - x) (c - x)$$
 (2.39)

This equation is easily integrated by decomposing the fraction into three partial fractions. The result may be written thus:

$$k_{\mathrm{III}}t = \frac{1}{(a-b)(b-c)(c-a)} \ln \left\{ \left(\frac{a}{a-x}\right)^{b-c} \left(\frac{b}{b-x}\right)^{c-a} \left(\frac{c}{c-x}\right)^{a-b} \right\}$$

# 2.4. Methods of Measurement of Reaction Rates and of Determination of Reaction Order

In accordance with the definition (Sec. 1.2), the determination of the reaction rate (or velocity) boils down to determining the dependence of the concentration of the substance on time. This task is solved with the aid of methods of quantitative analysis most suitable for a given concrete case.

The analytical methods used in kinetics may be classified into two categories—chemical and physical. Chemical analysis makes it possible to determine directly the concentration of one of the reacting substances or reaction products (see Table 2.3). The difficulty in the use of chemical analysis is associated with the necessity of the results being quickly compared with the reaction under study. If this is impossible because of the procedure being too slow, the reaction has to be stopped (it is "frozen") by sharply changing one of the reaction conditions—the temperature is lowered, the catalyst is removed, an inhibitor is added, etc. Chemical methods of analysis have the advantage of providing absolute values of concentration.

Physical methods of analysis are usually more convenient than chemical methods: a physical property of the reaction mixture that undergoes change during the course of the reaction is measured. Obviously, there must be a substantial difference in the contributions to the measured property of the reactants and products. Among physical methods the following may be mentioned: methods associated with pressure measurements in gaseous reactions (see Table 2.1); dilatometry, i.e., the measurement of the change in the volume produced by reaction; optical methods such as polarimetry, refractometry, and also colorimetry. Electrical methods of analysis (electroanalysis) are also employed: conductimetry, potentiometry, polarography, and mass spectroscopy. Theoretically, any property that undergoes sufficient change may be used to follow the course of the reaction. Much less frequently used are such physical methods as measurement of heat conductivity, freezing point, viscosity (for polymerization reactions), and also of the reaction heat.

An advantage of physical methods is, as a rule, their rapidity. They also make it possible to obtain a larger number of experimental points in a given time interval. The measurements can often be performed directly in the reaction vessel, so that sampling and the errors that arise during this procedure are excluded. Ordinarily, a physical measurement has no effect on the state of the system. Also, continuous automatic recording of the changes of a property can often be employed. Physical methods, however, do not yield absolute values of concentration. Besides, there may arise errors associated with the reaction itself. For example, in a spectroscopic study, small amounts of strongly coloured contaminants or by-products may distort the picture considerably. Therefore, not one but a combination of several methods should be used for a complete study of a reaction. This is especially desirable when the stoichiometry of the reaction is to be tested.

The Relation Between Physical Properties and Concentrations. As known, one of the requirements put forth to a physical property taken as a criterion of the extent of reaction consists in that its values must be substantially different for reactants and products. Another requirement to this property is that it must be

associated in some simple manner with the concentrations of the reactants and products. The most convenient in this sense is a linear relationship between physical properties and concentration, say, between the concentration, on the one hand, and the electrical conductivity, optical density, rotation of the plane of polarization and the pressure of gases, on the other. In dilute solutions, many other physical properties are also linearly dependent on concentration: specific volume, refractive index, vapour pressure, fluidity, etc. These linear relationships are however often violated when attempts are made to apply them to a very wide range of concentrations. Caution must be exercised in such cases.

There can be derived a general equation relating the physical property being measured to the concentration for a case of their linear relationship. Let us consider a reaction in a general form:

$$v_1A + v_2B + v_3C \longrightarrow v'F$$
 (2.40)

where F includes all the products. Let  $\lambda$  be the value of the physical property at time t:

$$\lambda = \lambda_{\text{medium}} + \lambda_{\text{A}} + \lambda_{\text{B}} + \lambda_{\text{C}} + \lambda_{\text{F}}$$
 (2.41)

where the first term on the right-hand side of the equation is the contribution of the medium, and the remaining ones depend on the concentrations; for example,

$$\lambda_{\mathbf{A}} = k_{\mathbf{A}} \left[ \Lambda \right] \tag{2.42}$$

 $k_{\rm A}$  being the proportionality factor.

Now let the initial concentrations of the substances be a, b, and c, and x the number of equivalents that have reacted in time t. Then

$$\lambda = \lambda_{\text{medium}} + k_{A} (a - v_{1}x) + k_{B} (b - v_{2}x) + k_{C} (c - v_{3}x) + k_{F}v'x \qquad (2.43)$$

and

$$\lambda_0 = \lambda_{\text{medium}} + k_{\text{A}}a + k_{\text{B}}b + k_{\text{C}}c \tag{2.44}$$

and also

$$\lambda_{\infty} = \lambda_{\text{medium}} + k_{\text{B}} (b - v_2 a/v_1) + k_{\text{C}} (c - v_3 a/v_1) + (k_{\text{F}} v' a/v_1)$$
 (2.45)

where  $\lambda_0$  and  $\lambda_\infty$  are the initial and final values of the property  $\lambda$ . In deriving Equation (2.45) it is assumed that substance A has been taken in a limited amount and is absent from the final system. Subtracting Equation (2.44) from Equation (2.45), we obtain:

$$\lambda_{\infty} - \lambda_{0} = k_{F} \frac{v'a}{v_{1}} + k_{A}a - k_{B} \frac{v_{2}a}{v_{1}} - k_{C} \frac{v_{3}a}{v_{1}}$$
 (2.46)

We also subtract (2.44) from (2.43):

$$\lambda - \lambda_0 = k_F v' x - k_A v_1 x - k_B v_2 x - k_C v_3 x \tag{2.47}$$

Now we can write:

$$\lambda - \lambda_0 = x \, \Delta k, \quad \lambda_\infty - \lambda_0 = (a/v_1) \, \Delta k$$
  
 $\lambda_\infty - \lambda = (a/v_1 - x) \, \Delta k$ 

where

$$\Delta k = k_{\mathrm{i}} \mathbf{v}^{\mathrm{T}} - k_{\mathrm{A}} \mathbf{v}_{\mathrm{I}} - k_{\mathrm{B}} \mathbf{v}_{\mathrm{2}} - k_{\mathrm{C}} \mathbf{v}_{\mathrm{3}}$$

From these relations we can obtain formulas useful in kinetics:

$$\frac{v_1 x}{a} = \frac{\lambda - \lambda_0}{\lambda_\infty - \lambda_0} \tag{2.48}$$

$$\frac{a}{a - v_1 x} = \frac{\lambda_\infty - \lambda_0}{\lambda_\infty - \lambda} \tag{2.49}$$

The variable measured may also be used to express  $b - v_2x$  and  $c - v_3x$ :

$$\frac{b}{b - v_2 x} = \frac{(b/a) (\lambda_{\infty} - \lambda_0)}{(b/a) (\lambda_{\infty} - \lambda_0) - (v_2/v_1) (\lambda - \lambda_0)}$$
(2.50)

It is clear that all these formulas simplify considerably when use is made of equivalent concentrations of the reactants (when  $b/a = v_2/v_1$ , etc.).

When the reaction does not go to completion, the data required can be obtained by calculations if the equilibrium constant is known.

One of the most frequently used methods of studying gas phase reactions is the manometric method mentioned earlier (see Sec. 2.1) in connection with the decomposition of acetone. Direct pressure measurements in the system are possible if the number of moles of gaseous substances undergoes change during the course of the reaction, as, for example, in the decomposition of phosgene:

$$COCl_2 = CO + Cl_2$$

The pressure gauge is also used when the reaction product is continuously removed by its absorption or condensation. For instance, in the reaction

$$H_2 + Cl_2 = 2HCl$$

hydrogen chloride can be absorbed by water.

Table 2.6 presents the results of pressure measurements for the decomposition of *tert*-butyl peroxide conducted in a static system. The reaction yields mainly acetone and ethane:

$$(CH_3)_3COOC(CH_3)_3 = 2(CH_3)_2CO + C_2H_6$$

According to this equation, when the reaction is complete, the pressure must increase by three times. In actual fact, it increases only by 2.88 times because of the formation of other products,

Time,	Total pressurc, P, mm Hg	$P_{\infty}-P$	k×10⁴, sec <sup>-1</sup>	Time, min	Total pressure, P, mm Hg	$P_{\infty}$ - $P$	$k \times 10^4$ , sec <sup>-1</sup>
0	173.5	318.3		12	244.4	247.4	3.44
2	187.3	304.5	3.58	14	254.5	237.3	3.32
3	193.4	298.3		15	259.2	232.5	3.43
5	205.3	286.5	3.39	17	268.7	223.1	3.43
6	211.3	280.5	3.42	18	273.9	217.9	<b>3.</b> 60
8	222.9	268.9	3.50	20	282.0	209.7	3.45
9	228.6	263.2	3.45	21	286.9	204.9	3.42
11	239.8	251.9	3.61	∞	491.8	201.0	0.12

TABLE 2.6. The Decomposition of tert-Butyl Peroxide at 154.6 °C

Average . . . .  $3.46 \pm 0.07$ 

The constants have been calculated for successive three-minute intervals.

The values of total pressure given in Table 2.6 include also certain low partial pressures of nitrogen used when the peroxide is introduced into the reaction vessel. Neglecting this, we use formulas (2.48) and (2.49):

$$\frac{x}{a} = \frac{P - P_0}{P_{\infty} - P_0}, \quad \frac{a - x}{a} = \frac{P_{\infty} - P}{P_{\infty} - P_0}$$

Assuming the decomposition of the peroxide to be first-order, we use formula (2.4) in the following form:

$$t = \frac{1}{k} \ln (P_{\infty} - P_{0}) - \frac{1}{k} \ln (P_{\infty} - P)$$
 (2.51)

According to Equation (2.51), if the assumption that the reaction is first order is valid, then  $\log{(P_{\infty} - P)}$  must be a linear function of time. Figure 2.4 shows that this is actually the case. Besides, Table 2.6 lists the values of the first-order rate constants calculated for successive three-minute intervals from the formula:

$$k = \frac{1}{t - t'} \ln \frac{P_{\infty} - P'}{P_{\infty} - P}$$

That the values of k remain constant within the accuracy of the experiment and the absence of their systematic "course" are also evidence that the reaction is first order. The average value of the constant given in Table 2.6 coincides with the value obtained by multiplying the slope of the straight line in Fig. 2.4 by 2.303. In first-order reactions (and this is their specific feature) the initial concentration need not to be known—the value of  $P_0$  must not necessarily be used in calculations. One may point out that in

the experiments used the initial pressure has not been measured at all and has been determined by extrapolation to t=0. A question arises as to the possibility of using the theoretical value of  $P_{\infty}$  (which is equal to  $3P_0$  for the decomposition of the peroxide) instead of the experimental limiting value of pressure. In the case under consideration, this would have given rise to a difference of several per cent in the rate constants over the pressure range under study. It is usually more preferable to use the experimental

value of  $P_{\infty}$  in calculations if only no anomaly is observed or experimental errors are unavoidable. For instance, if the reaction does not go to completion because of the established equilibrium, this must be taken into account in introducing appropriate corrections into the value of  $\lambda_{\infty}$ . The relatively slow secondary reactions of the products may also lead to an erroneous value of  $\lambda_{\infty}$ . In such a case it is better to use the theoretical value of  $P_{\infty}$ .

We shall now examine a more complicated case of the calculation of the rate of a gas reaction

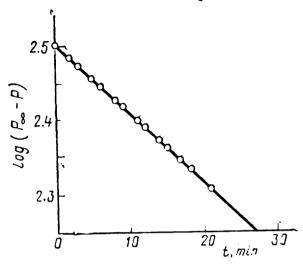


Fig. 2.4. The straight-line dependence proves the first order of the reaction of decomposition of ditert-butane peroxide (after Releigh, Rast, and Fogan).

when corrections must be introduced into each pressure measurement. The condensation of acrolein with 1,3-butadiene leading to the formation of tetrahydrobenzaldehyde

has been studied by Kistiakowsky and Lacher at 291.2 °C. The course of this reaction is complicated by the simultaneous occurrence of a second-order reaction (the dimerization of butadiene):

$$2C_4H_6 = C_8H_{12}$$

Table 2.7 gives the values of the total pressure in the system at various times, beginning from the known initial pressure of acrolein and butadiene. These data were then used to calculate the changes in the pressure of acrolein and butadiene for each successive time interval. This was done in the following way. First, the change in the pressure due to dimerization of butadiene is determined approximately:

 $\Delta P_{\rm dim} = k' [P_{\rm but}]^2 \Delta t$ 

Time, sec	Ptot	$-\Delta P$	$-\Delta P_{ m dim}$	Pacr	Pbut	$\begin{array}{c} k \times 10^{7} \\ \text{mm} & \text{sec} \end{array}$
0	658.2	6.1	0.2	418.2	240.0	
63	652.1	10.7	0.3	412.3	233.7	9.6
181	641.4	17.3	0.5	401.9	222.7	9.6
384	624.1	11.9	0.3	385.1	204.9	9.9
542	612.2	14.1	0.3	373.5	192.7	9.7
745	598.1	11.0	0.3	359.7	178.3	10.0
925	587.1	12.2	0.3	349.0	167.0	9.7
1145	574.9	10.8	0.3	337.1	154.5	9.8
1374	564.1	11.3	0.2	326 6	143.4	9.3
1627	552.8	13.4	0.3	315.5	131.9	9.9
1988	539.4			302.4	118.2	9.4
ı	ı	•		I	' A <b>v</b> erage .	9.7

TABLE 2.7. The Condensation of Acrolein with Butadiene at 291.9 °C (pressure in mm Hg)

where  $P_{\rm but}$  is the partial pressure of butadiene at the beginning of the given time interval, and k' is the preliminarily determined rate constant for the dimerization. Then  $\Delta P_{\rm dim}$  is subtracted from  $\Delta P_{\rm tot}$  and this gives the drop in pressure due to the main reaction. From the stoichiometry of both reactions it follows that

$$\Delta P_{\rm acr} = \Delta P_{\rm tot} - \Delta P_{\rm dim} \tag{2.52}$$

(where  $\Delta P_{acr}$  is the drop of the partial pressure of acrolein),

$$\Delta P_{\text{but}} = \Delta P_{\text{tot}} + \Delta P_{\text{dim}} \tag{2.53}$$

so that the pressure values at the end of each time interval can be found. These values are also given in Table 2.7. The rate constants listed in the last column have been calculated on the assumption of the second order of the main reaction from the unintegrated form of the kinetic equation

$$-\frac{\Delta P_{\text{acr}}}{\Delta t} = k \left( P_{\text{acr}} \right) \left( P_{\text{but}} \right) \tag{2.54}$$

by using the average values of partial pressures for a given time interval. As seen from Table 2.7, the second-order rate constant exhibits satisfactory constancy and, hence, the assumption of the second-order of the reaction under study is justified. The average value of the rate constant is  $9.7 \times 10^{-7}$  mm<sup>-1</sup>·sec<sup>-1</sup>. Another method of kinetic treatment may also be used. We may write an integrated formula [see Equation (2.27)] in the following form

for the reaction under study:

$$kt = \frac{1}{P_{\text{acr}}^{\circ} - P_{\text{but}}^{\circ}} \ln \frac{P_{\text{acr}}}{P_{\text{but}}} + \text{const}$$
 (2.55)

and then use the graphic method. Figure 2.5 is a plot of  $log[P_{acr}/P_{but}]$  versus time; its linearity too proves convincingly the second order of the reaction (page 43). The slope of the straight line multiplied by 2.3 and divided by (418.2 — 240.0) gives  $k = 10.9 \times 10^{-7}$  mm<sup>-1</sup>·sec<sup>-1</sup>, i.e., a value somewhat different

from that given in Table 2.7. The difference between the values of the constants, 10.9 and 9.7, is partly due to the dimerization reaction, which is included in the overall rate when calculated by formula (2.55). On the other hand, this difference is also due to the difference arising because of the use of the integrated and unintegrated forms of the rate equation.

Let us also consider some examples of the study of reactions in solutions. Here, along with the chemical method of analysis and measurements based on the rate of evolution or absorption of

0.32 0.32 0.32 0.32 0.32 0.56 

Fig. 2.5. The straight-line dependence proves the second order of the condensation of acrolein with butadiene (after Kistiakowsky and Lacher).

a gas, three analytical methods are most widely employed: colorimetry (or spectrometry), conductimetry, and dilatometry. We shall consider one example for each of these methods.

If a reaction proceeds with a change in the number or type of ions and is associated with a change in the electrical resistance, then the course of the reaction can be followed by measuring the resistance of the solution. Here it is convenient to use an a-c direct-reading bridge and an oscillograph as a null instrument. This requires that the temperature be maintained sufficiently constant; the temperature is controlled to an accuracy of 0.03° by means of ordinary thermostats. There are well-known limitations to the application of this method. Thus, the solvent used must have a high dielectric constant and a sufficiently high solvating power. Otherwise, the resistance and concentration will not be interrelated in a simple manner.

Since the resistance is inversely proportional to the electrical conductance, which in its turn is proportional to concentration, the principal equations to be used for studying kinetics by

measuring the resistance may be given in the form:

$$\frac{x}{a} = \frac{1/R - 1/R_0}{1/R_\infty - 1/R_0} = \frac{(R_0 - R) R_\infty}{R (R_0 - R_\infty)}$$
(2.56)

$$\frac{a}{a-x} = \frac{1/R_{\infty} - 1/R_{0}}{1/R_{\infty} - 1/R} = \frac{(R_{\infty} - R_{0})R}{R_{0}(R_{\infty} - R)}$$
(2.57)

Table 2.8 contains some data for the reaction of pyridine with phenacyl bromide leading to the formation of a quaternary ammonium salt, phenacyl-pyridine bromide.

TABLE 2.8. Phenacyl Bromide and Pyridine in Methanol (temperature 35.0 °C, concentration 0.0385 mole/litre)

Time, min	Resistance, ohm	$-R/(R_{\infty}-R)$	Time, min	Resistance, ohm	$ -R/(R_{\infty}-R) $
7	45,000	1.019	110	5100	1.186
28	11,620	1.074	127	4560	1.213
53	9200	1.096	153	3958	1.253
68	7490	1.120	203	3220	1.330
84	6310	1.145	368	2182	1.580
99	5537	1.170	∞	801	

k = 0.0445 litre·mole<sup>-1</sup>·min<sup>-1</sup>.

The reaction was conducted in methanol solution; since neutral molecules form ions, the resistance falls off rapidly as the reaction proceeds:

In studying the kinetics, use was made of equal concentrations of the reactants (0.0385 mole/litre), in which case the simplest kinetic formula (2.15) is applicable on the assumption of second order; this formula may be put in the form

$$t = \frac{1}{ak} \cdot \frac{a}{a - x} - \frac{1}{ak} \tag{2.58}$$

or in terms of resistance:

$$t = \left(\frac{1}{ak} \cdot \frac{R_{\infty} - R_0}{R_0}\right) \frac{R}{R_{\infty} - R} - \frac{1}{ak} \tag{2.59}$$

According to these equations, if the assumption of the secondorder of the reaction holds true, 1/(a-x) or  $R/(R-R_{\infty})$  must be a linear function of time. Figure 2.6 shows that this is actually the case. The rate constant is found in this case by dividing the slope of the straight line in Fig. 2.6 by the initial concentration a and by the y-intercept equal to  $R_0/(R_0-R_\infty)$ . True, in this particular case, this relation is very close to unity since  $R_0$ , i.e., the resistance at the initial moment, is very high. It may also be noted that in this case the exact value of  $R_0$  is immaterial—one can calculate x or (a-x) for any time from the y-intercept and the final resistance, using Equations (2.58) and (2.59).

Further, let us consider, as an example of the spectroscopic study of kinetics, the interaction of styrene dichloride with

ethanol:

$$C_6H_5CH=CH-CHCl_2 + C_2H_5OH \longrightarrow C_6H_5-CH-CH=CHCl + HCl OC_2H_5$$

Styrene chloride contains a double bond conjugated with a benzene ring and absorbs strongly in the region of 2600 Å, whereas the product (1-chloro-3-ethoxy-3-phenyl-1-propylene) does not contain such a conjugation and does not absorb up to the region of 2100 Å. Accordingly, the measurement of optical density

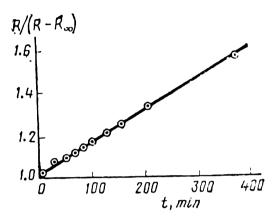


Fig. 2.6. The second-order reaction between phenacyl bromide and pyridine at equal initial concentrations of the reactants.

at 2600 Å as a function of time may serve as a tool in studying kinetics. These measurements are conveniently performed with the

TABLE 2.9.	Styrene	Chloride	in	Absolute	Ethanol	at :	22.6 °	°C
$([RCl_2] = 2$	2.11×10-	5 mole/iit	re;	[NaOEt] =	= 0.547  r	nole	/litre	e)

Time, min	Optical density D at 2600 Å	$k \times 10^3$ , min <sup>-1</sup>	Time, min	Optical density D at 2600 Å	$k \times 10^3$ , min-1
0 10 31 74	0.406 0.382 0.338 0.255	6.0 5.8 6.3	127 178 1200	0.184 0.143 0.01	6.0 5.8

D = elc, where e is the molar absorption coefficient and l is the thickness of the absorbing layer, and c is the molar concentration

aid of a photoelectric spectrophotometer. But in the case of a relatively slow reaction, samples can be removed from the thermostated reaction vessel. Table 2.9 gives the data obtained by Andrew for the reaction under discussion. The reaction mixture contained sodium alkoxide, but the rate of the reaction did not

depend on its concentration. The rate constant was calculated on the assumption of first order from the formula

$$k = \frac{2.303}{t} \log \left(\frac{D_0}{D}\right) \tag{2.60}$$

which is obtained from the following more exact formula:

$$k = \frac{2.303}{t} \log \frac{D_{\infty} - D_0}{D_{\infty} - D} \tag{2.61}$$

since  $D_{\infty}$  is very small. As seen from Table 2.9, the assumption of a first-order reaction is justified.

The dilatometric method may be employed provided only that the reaction is accompanied by a change in volume. According to the data obtained by Kilpatrick *et al.*, the hydration of isobutylene to give isobutyl alcohol, which is catalyzed by hydrogen ions,

$$CH_3$$
  $CH_3$   $CH_3$ 

is accompanied by a decrease in volume. The course of this reaction can be traced by measuring the level of the liquid in the capillary connected with a sufficiently large vessel containing the reaction mixture. During these measurements the temperature must be kept constant to an accuracy of up to a thousandth of a degree.

TABLE 2.10. The Hydration of Isobutylene in a Solution of Perchloric Acid (t = 25 °C: [HClO<sub>4</sub>] = 0.3979 mole/litre; [isobutylene] = = 0.00483 mole/litre)

Time, min	Measurement by dilatometer at time t	At t + 120 min	Time, min	Measurement by dilatometer at time t	At t + 120 min
0 5 10	18.84 18.34 17.91	13.50 13.42 13.35	25 30 35	16.86 16.56 16.27	13.12 13.05 13.00
15 20	17.53 17.19	13.27 13.19	∞	16.00	12.94

Table 2.10 presents two series of measurements of the level in the dilatometer expressed in arbitrary units and taken in a two-hour interval. Assuming the concentrations of water and hydrogen ions to be constant and the reaction to be first order in isobutylene, the authors plotted a graph of  $\log(V-V_{\infty})$  versus time (Fig. 2.7). The slope of the straight line when multiplied by 2.303 gave a first-order rate constant equal to  $1.322 \times 10^{-2}$  min<sup>-1</sup>.

Here we should speak of a pseudo-first-order reaction since it involves water and the rate depends on the concentration of the acid. It may be added that if the thus observed rate constant is divided by the hydrogen-ion concentration, we shall obtain a second-order rate constant independent of the concentration of the acid (provided that the ionic strength of the solution is kept constant).

From the examples presented in this section it may be concluded that one of the methods of determining the reaction order is

the substitution of the results of measurements of any physical variable at different times into one of the kinetic equations with the purpose of obtaining a series of values of the rate constant, exhibiting satisfactory constancy (Tables 2.6, 2.7, and others). Another method of determining the reaction order is the derivation of an expression linearly dependent on time and the calculation of the constant from the slope (Figs. 2.4 through 2.7).

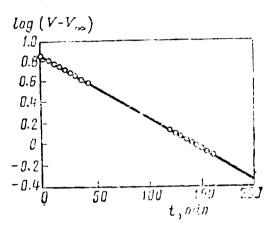


Fig. 2.7. The hydration of isobutylene has a pseudo-first order.

One of the direct methods of determining reaction order is based on the study of the dependence of the half-life on the initial concentration and is applicable if the kinetic equation has the form:

$$\frac{dx}{dt} = k (a - x)^n \tag{2.62}$$

As is already known (see Table 2.4), at n = 1 the half-life period

$$T_{1/2} = \frac{\ln 2}{k} \tag{2.63}$$

and for  $n \neq 1$ :

$$T_{1/2} = \frac{2^{n-1} - 1}{k(n-1) a^{n-1}} \tag{2.64}$$

Based on these relations, we can represent the dependence of the half-life on the initial concentration in the following form:

$$T_{1/2} = \int (n, k)/a^{n-1} \tag{2.65}$$

where f is a certain function of n and k is the constant for the given reaction at constant temperature. Taking logarithms in Equation (2.65), we obtain the relation:

$$\log T_{1/2} = \log f - (n-1) \log a \tag{2.66}$$

which indicates that  $\log T_{1/2}$  must be linearly dependent on the logarithms of the initial concentration and the slope of the straight line is equal to n-1.

A variant of the method may be employed, which is based on the use of two quantities,  $T_{1/2}$  and  $T'_{1/2}$ , for two values of initial concentrations, a and a'. From two expressions of the type (2.66) we obtain the following equation for the reaction order:

$$n = 1 + \frac{\log T'_{1/2} - \log T_{1/2}}{\log a - \log a'}$$
 (2.67)

which is suitable for direct calculation of the reaction order from the data of two experiments conducted at sufficiently differing

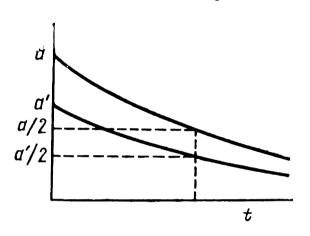


Fig. 2.8. A graph illustrating that the half-life period is independent of the initial concentration for a first-order reaction.

initial concentrations. For the first order, the half-life period does not depend on the initial concentration, which is illustrated by Fig. 2.8.

Equations (2.63) and (2.67) can be generalized if we consider the time,  $T_y$ , of conversion of a fraction y of the starting material. If the concentration decreases from a to a(1-y), then Equation (2.66) will assume the form:

$$\log T_y = \log f + (n - 1) \log a \quad (2.67a)$$

and, generally speaking, the relation between  $\log T_y$  and  $\log a$  must be linear. A more general expression may also be written instead of Equation (2.67):

$$n = 1 + \frac{\log T_y' - \log T_y}{\log a - \log a'}$$
 (2.68)

We have so far described methods of determining the reaction order, which call for two or more experiments with different initial concentrations. But, evidently, we can use, in an analogous manner, two or more time intervals during the course of a single experiment if the reactant concentration at the beginning of each time interval is taken as the initial concentration. In Fig. 2.9,  $t_1$  corresponds to a(1-y), and  $t_2$  corresponds to the concentration  $a(1-y)^2$ . Thus,  $T_y' = t_2 - t_1$  and Equation (2.68) takes the form:

$$n = 1 + \frac{\log\left[(t_2/t_1) - 1\right]}{\log\left[1/(1 - y)\right]} \tag{2.69}$$

In Fig. 2.9, 
$$t_2/t_1 = 3$$
 and  $y = 1/2$ , so that  $n = 1 + \log 2/\log 2 = 2$ 

It should be stressed once again that the method under discussion is applicable only if the kinetic equation has the form (2.62). This equation may however be generalized in the following fashion.

Let the kinetic equation be specified in the form:

$$\frac{dx}{dt} = k \left[ A \right]^p \left[ B \right]^q \left[ C \right]^r \tag{2.70}$$

where [A], [B], and [C] are, respectively, the concentrations of the substances A, B, and C. Conditions can in principle be created, which will facilitate the determina-

tion of the reaction order.

Suppose that the concentrations of all the substances, with the exception of A, remain constant during the course of the reaction, in which case the reaction will have a pseudo order p. In practice, the required constancy of the concentrations of B, C, ... can be attained by taking a large excess of these substances as compared with substance A. We can now

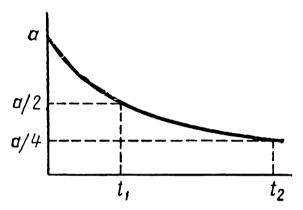


Fig. 2.9. Two successive half-life periods for a second-order reaction,  $t_2 = 3t_1$ .

introduce a new constant for the given experiment:

$$k = k \left[ \mathbf{B} \right]^q \left[ \mathbf{C} \right]^r \tag{2.71}$$

Now Equation (2.70) is written in the following form:

$$\frac{dx}{dt} = k' \left[ A \right]^p \tag{2.72}$$

Equation (2.72) coincides functionally with Equation (2.62). Thus, formulas (2.67) through (2.69) become again applicable if of course the appropriate notation is used. In principle, in this way we can find the reaction order with respect to each of the reacting substances or even with respect to the reaction product if the latter affects the rate of the reaction.

Another method used to simplify Equation (2.70) consists in selecting such concentrations of the reactants that during the course of the experiment they remain in unchanged proportions. For example, if in the reaction

$$2NO + O_2 = 2NO_2$$

the molar concentration or partial pressure of NO is two times higher than that of  $O_2$ , then the reactants are present in equivalent amounts. For the equation of the reaction in a general form (2.70), with the conditions of constant proportions formulated,

we may write:

[B] = 
$$\rho_1$$
 [A], [C] =  $\rho_2$  [A] (2.73)

where  $\rho_1$  and  $\rho_2$  are the constants determined by the values of the stoichiometric coefficients. Now Equation (2.70) assumes the form:

$$\frac{dx}{dt} = k\rho_1^q \rho_2^r [\Lambda]^{p+q+r} \tag{2.74}$$

or

$$\frac{dx}{dt} = k'' (a - x)^n$$

Here a new constant is introduced, namely,  $k'' = k\rho_1^q \rho_2^r$ , and n = p + q + r is the overall kinetic order of the reaction. Equation (2.74) is reduced to (2.62), and the "half-conversion method" becomes again applicable. There is however an important limitation to the use of the latter variant. It excludes the study of the effect of the products on the rate since their concentration cannot remain proportional to the concentration of the reactant during the course of the experiment.

Van't Hoff proposed the obviously simplest use of Equation (2.70), which consists of a direct comparison of the reaction rate and the concentration. First, the rate of the reaction is approximately estimated by replacing the derivative dx/dt by the difference quotient  $\Delta x/\Delta t$ . Further, the rate is measured at two values of the initial concentrations of one of the reactants, say B, the concentrations of the other reactants being kept constant. Then, proceeding from Equation (2.70), we may write:

$$\left(\frac{\Delta x}{\Delta t}\right)_{1} \approx \left(\frac{dx}{dt}\right)_{1} = (k [A]^{p} [C]^{r}) [B]_{1}^{q}$$
$$\left(\frac{\Delta x}{\Delta t}\right)_{2} \approx \left(\frac{dx}{dt}\right)_{2} = (k [A]^{p} [C]^{r}) [B]_{2}^{q}$$

Dividing the first of these equations by the second, taking logarithms and solving the result for q, we obtain the van't Hoff equation:

$$q = \frac{\log (dx/dt)_1 - \log (dx/dt)_2}{\log |B|_1 - \log |B|_2}$$
 (2.75)

Or

$$q = \frac{\log (w_1/w_2)}{\log [B]_1/[B]_2}$$

where  $w_1$  and  $w_2$  are the rates at the concentrations  $[B]_1$  and  $[B]_2$ . We may cite an example of the combined use of Equations (2.75) and (2.66). The thermal decomposition of tetrahydrofuran

in the gas phase is a complex reaction leading to the formation of a number of products. The data obtained by measurements of the pressure as a function of time do not correspond to any simple integer order. Accordingly, a series of experiments have been accomplished, in which the maximum rates,  $(\Delta P/\Delta t)_{\rm max}$ , and also the half-life periods for different initial pressures,  $P_0$ , were determined. The construction of a plot of  $\log (\Delta P/\Delta t)_{\rm max}$  versus  $\log P_0$  gave a straight line with a slope of 1.5. A straight line was also obtained for the relation between  $\log T_{1/2}$  and  $\log P_0$  but with slope equal to -0.55. These data point to the reaction order equal to 1.5.

# Application of the Basic Law of Kinetics to Complex Reactions

Chemical reactions that proceed from reactants to products through two or more intermediate steps with the participation of the same reactants are called **complex reactions**. The kinetics of complex reactions is studied by using the **principle of independency** which is in fact one of the postulates of chemical kinetics: if several reactions take place in a system, then each of these reactions obeys the basic kinetic law and proceeds independently of the other reactions. The complete change of the system is the sum of these independent changes.

The principle of independency is not of course general since it is known that reactions may have an effect on one another, say, in induced reactions. In many cases, however, the principle of independency is confirmed by experiment and its application is fruitful.

### 3.1. Reversible or Opposing Reactions

First-Order Reversible Reactions. Let the reversible reaction

$$A \Longrightarrow B$$

be first order in both directions. Let a and b be the initial concentrations of the reactant and product, and x, as before, the decrease in concentration of the reactant by time t.

The rate constants are designated as follows: for the forward reaction,  $k_1$  instead of  $k_1'$  and  $k_2$  instead of  $k_1''$ . Then, according to the principle of independency, the overall observed rate of the reaction will be the sum of the independent rates of the forward and reverse reactions. Namely,

$$\frac{dx}{dt} = k_1 (a - x) - k_2 (b + x) \tag{3.1}$$

The most substantial difference between the type of reactions under discussion and those considered so far consists in that in the limit  $(t \to \infty)$  they do not go to completion, when  $x \to a$ , and

proceed only until a state of equilibrium is attained, when the overall rate of the reaction becomes equal to zero:

$$\frac{dx}{dt} = k_1 (a - x_{\infty}) - k_2 (b + x_{\infty}) = 0$$

Here  $x_{\infty}$  is the change in concentration, which corresponds to the equilibrium.

From what has been said above follows, in fact, the definition of the concept of chemical equilibrium as the mobile, dynamic equilibrium determined by the equality of the rates of the forward and reverse reactions. Rearranging the equilibrium condition, we have:

$$\frac{b+x_{\infty}}{a-x_{\infty}} = \frac{k_1}{k_2} = K_c \tag{3.2}$$

Evidently, the left-hand side of this equality is the ratio of the equilibrium concentrations and  $K_c$  is the equilibrium constant expressed in terms of concentration and introduced in a different way in thermodynamics. Thus, the equilibrium constant is equal to the ratio of the rate constants of the forward and reverse reactions. In studying the kinetics of reversible reactions it is helpful to make use of the equilibrium relations, which is what we shall exactly do in integrating Equation (3.1). Rearrangement of this equation gives:

$$\frac{dx}{dt} = k_1 a - k_1 x - k_2 b - k_2 x = (k_1 + k_2) \left( \frac{k_1 a - k_2 b}{k_1 + k_2} - x \right)$$
(3.3)

Setting dx/dt to zero, i.e., using the equilibrium state, it is easy to see that

$$\frac{k_1a - k_2b}{k_1 + k_2} = x_{\infty}$$

Thus, the differential rate equation will take the form:

$$\frac{dx}{dt} = (k_1 + k_2) (x_\infty - x)$$

Separating the variables and integrating between limits from 0 to t and from 0 to x, we obtain the formula

$$\ln \frac{x_{\infty}}{x_{\infty} - x} = (k_1 + k_2) t \tag{3.4}$$

which is very similar to the first-order formula (2.4), the only difference being that here  $x_{\infty}$  is used instead of the initial concentration a and, on the right-hand side, instead of one constant  $k_1$  we have the sum of the first-order rate constants of the forward and reverse reactions.

There are many such reactions, especially in solutions. As an illustration may be taken the reactions of cis-trans isomerization,

say, of stilbene:

$$C_6H_5CH=CHC_6H_5$$
 (cis)  $\subset$   $C_6H_5CH=CHC_6H_5$  (trans)

Well-known reactions of this type are the isomerization of ammonium cyanate into carbamide (urea) in aqueous solution:

and the so-called mutarotation (change of rotation) of glucose. Glucose is known to exist as two stereoisomers,  $\alpha$  and  $\beta$ , which rotate the plane of polarization differently:

In one of the experiments conducted at 20 °C, the freshly prepared solution of pure  $\alpha$ -glucose rotated the plane of polarization by  $+113^{\circ}$ . With the lapse of time the angle of rotation decreased and reached the limiting value  $+52.2^{\circ}$  which did not change with time. In a solution of originally pure  $\beta$ -glucose, the angle of rotation changes from  $+19^{\circ}$  to the same limiting value,  $+52.5^{\circ}$ . This phenomenon is easily explainable if we assume the dynamic isomerization of the two forms of glucose, i.e., the existence of a reversible reaction between them. No matter which form is the starting point, we eventually arrive at an equilibrium mixture of the two forms, which rotates the plane of polarization to the right by  $52.5^{\circ}$ .

Let us perform a simple calculation to determine  $x_{\infty}$ , assuming that the angle of rotation is proportional to the concentration of the rotating substance. The starting point is  $\alpha$ -glucose and its concentration is taken to be equal to unity. So,

$$\alpha$$
-Glucose  $\Longrightarrow$   $\beta$ -Glucose

$$\begin{array}{lll} \text{At the initial moment} & c_\alpha = 1 & c_\beta = 0 \\ t = 0 & \\ \text{At time } t & c_\alpha = 1 - x & c_\beta = x \\ \text{At time } t_\infty & c_\alpha = 1 - x_\infty & c_\beta = x_\infty \end{array}$$

The angle of rotation of the equilibrium mixture is summed up of two angles:

$$113(1 - x_{\infty}) + 19x_{\infty} = 52.5$$

This gives  $x_{\infty} = 0.65$ , i.e., the equilibrium mixture contains 65 per cent of the  $\beta$ - and 35 per cent of the  $\alpha$ -form. Now, assuming the reaction to be first order, we may write formula (3.4) thus:

$$\ln \frac{0.65}{0.65 - x} = (k_1 + k_2) t \tag{3.5}$$

The kinetic calculations can be made by substituting the values of x corresponding to various times into Equation (3.5). As has been found, the sum  $k_1+k_2$  exhibits good constancy, which supports the initial assumption of the first order of the two reactions. At 20 °C the average value of  $k_1 + k_2 = 1.46 \times 10^{-2}$  min<sup>-1</sup>. For the individual values of the rate constants to be determined, it is necessary to utilize the equilibrium constant:

$$K_c = \frac{k_1}{k_2} = \frac{x_\infty}{1 - x_\infty} = \frac{0.65}{0.35} = 1.86$$

Thus,

$$k_1 = 0.95 \times 10^{-2} \,\mathrm{min}^{-1}, \quad k_2 = 0.51 \times 10^{-2} \,\mathrm{min}^{-1}$$

Hence, at equal concentrations the rate of the forward reaction is nearly twice as high as that of the reverse reaction.

First- and Second-Order Reversible Reactions. Let us consider a more complicated case where the reaction is first order in the forward direction and second order in the reverse direction:

$$\begin{array}{ccc}
A & \xrightarrow{k_1} & B + C \\
a - x & x & x
\end{array}$$

Starting from one substance A, for time t we have concentrations placed below the corresponding symbols for the substances. The rate of the reaction at this moment is given by

$$\frac{dx}{dt} = k_1 (a - x) - k_2 x^2 = -k_1 \left( \frac{k_2}{k_1} x^2 + x - a \right) = -k_1 (\beta - x) (\gamma - x) \quad (3.6)$$

Here  $\beta$  and  $\gamma$  are the roots of the quadratic equation

$$\frac{k_2}{k_1} x^2 + x - a = 0$$

that is,

$$\beta, \gamma = -\frac{1}{2} \cdot \frac{k_1}{k_2} \pm \left[ \frac{1}{4} \left( \frac{k_1}{k_2} \right)^2 + \frac{k_1}{k_2} a \right]^{1/2} = -\frac{1}{2} \frac{k_1}{k_2} \pm \alpha$$
 (3.7)

where  $\alpha$  stands for the radical. Equation (3.6) is easily integrated by the method of decomposition into partial fractions:

$$\frac{1}{\beta - \gamma} \ln \frac{\beta (\gamma - x)}{\gamma (\beta - x)} = k_1 t \tag{3.8}$$

If the values of the roots  $\beta$  and  $\gamma$  from Eq. (3.7) are substituted into Eq. (3.8), we shall obtain the final integrated kinetic formula:

$$\frac{1}{2\alpha t} \ln \frac{a + x \left(\alpha \frac{k_2}{k_1} - \frac{1}{2}\right)}{a - x \left(\alpha \frac{k_2}{k_1} + \frac{1}{2}\right)} = k_1$$
 (3.9)

We can solve Eq. (3.9) for the degree of conversion (the extent of reaction) x/a

$$\frac{x}{a} = \frac{1 - e^{-2\alpha k_1 t}}{\left(\alpha \frac{k_2}{k_1} + \frac{1}{2}\right) + \left(\alpha \frac{k_2}{k_1} - \frac{1}{2}\right) e^{-2\alpha k_1 t}}$$
(3.10)

When t tends to infinity, the exponents turn into zero and x/a reaches a certain limiting value corresponding to the equilibrium:

$$\frac{x_{\infty}}{a} = \frac{1}{a \frac{k_2}{k_1} + \frac{1}{2}}$$

Substitution of an expression for  $\alpha$  into this equation gives the ratio of the equilibrium concentrations:

$$\frac{x_{\infty}^2}{a-x} = \frac{k_1}{k_2} = K_c$$

which can also be obtained directly by equating Eq. (3.6) to zero. A good example of reactions of this type is the reversible dissociation of nitrogen tetroxide:

$$N_2O_4 \stackrel{k_1}{\rightleftharpoons} 2NO_2$$

At 25 °C the rate constant for the forward reaction is  $k_1 = 5 \times 10^4 \, \mathrm{sec^{-1}}$ . The equilibrium constant is  $K_c = 5.4 \times 10^{-3}$  (mole/litre). Thus, the rate constant of the reverse reaction not measured directly under these conditions can be found from the following relation:

$$\frac{k_1}{K_c} = k_2 = \frac{5 \times 10^4}{5.4 \times 10^{-3}} = 9.3 \times 10^6 \text{ litre/mole} \cdot \text{sec}$$

Second-Order Reversible Reactions. Consider the classical example of the investigation of a second-order reversible reaction in both directions. This is the decomposition-formation of hydrogen iodide studied by M. Bodenstein as early as the end of last century. In his experiments Bodenstein placed the reactants in glass flasks, sealed them and analysed the contents after the flasks had been kept in a thermostat for a certain period of time.

In experiments on the decomposition of HI the flasks were filled with hydrogen iodide at 0 °C and 760 mm Hg. Therefore, the initial concentration of HI was 1 mole per 22.4 litres and it was this concentration unit that was used to calculate the constants.

Thus, for the reaction

2HI 
$$\frac{k_1}{k_2}$$
 H<sub>2</sub> + I<sub>2</sub>

the initial concentration of hydrogen iodide a at time t will decrease down to a-x and the concentrations of hydrogen and iodine will become equal to x/2. Assuming the reaction to be second order, we write down its rate at time t:

$$\frac{dx}{dt} = k_1 (a - x)^2 - k_2 \left(\frac{x}{2}\right)^2 \tag{3.11}$$

At the established equilibrium dx/dt = 0, i.e.,

$$k_1 (a - x_\infty)^2 = k_2 \left(\frac{x_\infty}{2}\right)^2 \tag{3.12}$$

where  $x_{\infty}$  is the decrease in concentration of HI, which corresponds to a state of equilibrium. Rearranging Eq. (3.12), we obtain the equilibrium constant  $K_c$ :

$$\frac{k_2}{k_1} = \frac{4 (a - x_\infty)^2}{x_\infty^2} = \frac{1}{K_c}$$
 (3.13)

Substituting  $k_2$  from Eq. (3.13) into Eq. (3.11), integrating and performing simple algebraic transformations, we obtain the integrated formula describing the course of the decomposition reaction:

$$k_{1} = \frac{2.303x_{\infty}}{2a (a - x_{\infty}) t} \log \left( \frac{2x_{\infty} - a}{a} \cdot \frac{\frac{ax_{\infty}}{2x_{\infty} - a} - x}{x_{\infty} - x} \right)$$
(3.14)

This formula was used by Bodenstein for calculating the constant  $k_1$  from the experimental data on the decomposition of HI. It was found that at constant temperature the constant  $k_1$  exhibits quite satisfactory constancy. Data were obtained for various temperatures (see Table 3.1), from which it is seen that the rate constant and the equilibrium constant increase with rise of temperature.

Experiments on the formation of hydrogen iodide were carried out in an analogous way. Known amounts of hydrogen and iodine were sealed up in cylinders which were allowed to stand for a certain time period in thermostats, after which the mixture was subjected to analysis. If the initial concentrations of the reactants in the reaction

$$H_2 + I_2 (gas) \xrightarrow{k_2} 2HI$$

<i>T</i> , K	$k_1, 2z.4$ litre-mole <sup>-1</sup> -min <sup>-1</sup>	k. litre-mole-1-sec-1	$K_s = \frac{k_1}{k_2}$
781	0.1059	0.0395	$ \begin{array}{c c} 2.9 \times 10^{-2} \\ 1.8 \times 10^{-2} \\ 1.5 \times 10^{-2} \\ 1.2 \times 10^{-2} \\ 7.9 \times 10^{-3} \end{array} $
700	0.00310	0.00116	$1.8 \times 10^{-2}$
666	0.000588	<b>0</b> .000220	$1.5 \times 10^{-2}$
629	0.0000809	0.0000302	$1.2 \times 10^{-2}$
556	0.000000942	0.000000352	$7.9 \times 10^{-3}$

TABLE 3.1. The Effect of Temperature on the Rate Constant of the Decomposition of HI

are denoted by a, b, and 0, and the concentrations at various elapsed times, i.e., those at time t, by  $a - \frac{x}{2}$ ,  $b - \frac{x}{2}$ , and x, then the rate equation will assume the form:

$$\frac{dx}{dt} = k_2 \left( a - \frac{x}{2} \right) \left( b - \frac{x}{2} \right) - k_2 K_C x^2 \tag{3.15}$$

Here the decomposition constant  $k_1$  is replaced by the product of the equilibrium constant  $K_c$  and the constant  $k_2$ . Integration of Eq. (3.15) yields an expression for  $k_2$  in terms of the experimental values of x at given times t:

$$k_2 = \frac{2 \times 2.303}{St} \log \frac{a+b-S}{a+b+S} \left\{ \frac{\frac{a+b+S}{1-4K_c} - x}{\frac{a+b-S}{1-4K_c} - x} \right\}$$
(3.16)

in which expression  $S = [(a + b)^2 - 4ab (1 - 4K_c)]^{1/2}$ .

Substituting into Eq. (3.16) the known equilibrium constant and x from the experiments on the formation, Bodenstein found the value of  $k_2$ .

Some examples of the determination of  $k_2$  for different a and b at a temperature of 666 K are listed in Table 3.2. As seen, the

t, min	а	ь	x	$k_2$ , 22.4 litre-mole <sup>-1</sup> -min <sup>-1</sup>
120	0.4081	0.2797	0.3239	0.0394
30	0.9086	0.6039	0.4448	0.0390
15	0.9086	2.2410	0.8076	0.0394

TABLE 32. Experiments on the Synthesis of Hydrogen lodide after Bodenstein

value of  $k_2$  exhibits satisfactory constancy. This in conjunction with the data given earlier proves that the reaction under study is really second order in both directions.

Experiments on the synthesis of HI were also conducted at different temperatures. The values of the rate constants obtained are presented in Table 3.3.

TABLE 3.3. The Effect of Temperature on the Rate Constant of the Formation of HI

Т. К	$k_2$ . 22.4 litre-mole <sup>-1</sup> -min <sup>-1</sup>	Т. К	$k_2$ , 22.4 litre-mole $-1$ -min $-1$
781 700 666	3.58 0.172 0.0370	629 556	0.00676 0.000119

More Complex Reversible Reactions. In the case of more complex reversible reactions, third order may appear. For instance, the oxidation of nitric oxide

$$2NO + O_2 \implies 2NO_2$$

is third order in the forward and second order in the reverse direction. The principles of mathematical treatment of the kinetics of this and other, more complex reactions are the same as before, but the complexity of the derived formulas naturally increases. Sometimes, the mathematical expressions obtained are hardly convenient for practical use and it is more expedient to resort to approximation methods for the study of kinetics.

#### 3.2. Parallel Reactions

In parallel reactions (concurrent reactions) the reacting substances, instead of proceeding along one path to yield a given set of products, also follow one or more other paths to give different products. We shall consider only the simplest cases, say, two parallel first-order reactions. A substance A takes part simultaneously in two reactions with the formation of products B and C:

$$\begin{array}{c} A \xrightarrow{k_1} & B \\ \xrightarrow{k_2} & C \end{array}$$

At the start of the reaction (t=0) only the substance A with a concentration a is present in the system; by time t the concentration becomes equal to a-x. Both reactions are considered to

be independent of each other and to obey the basic law of kinetics—the overall change of the concentration is made up of the sum of the independent changes:

$$\frac{dx}{dt} = k_1 (a - x) + k_2 (a - x) = (k_1 + k_2) (a - x) \tag{3.17}$$

It is easy to see that integration of this equation gives ordinary first-order formulas:

$$\ln \frac{a}{a-x} = (k_1 + k_2) t \tag{3.18}$$

or

$$a - x = ae^{-(k_1 + k_2)t} (3.19)$$

the only difference being that, instead of a single constant, they contain the sum of two first-order constants. As seen from Eqs. (3.18) and (3.19), the experimental values of x allow us to determine not the separate values of the constants  $k_1$  and  $k_2$  but their sum. Using the rates of accumulation of the products, we can however find the ratio  $k_1/k_2$ . Denoting the concentrations of the products as  $c_B$  and  $c_C$ , we write the following equation:

$$\frac{dc_{\rm B}}{dt} = k_1 (a - x) \quad \text{and} \quad \frac{dc_{\rm C}}{dt} = k_2 (a - x) \tag{3.20}$$

To reduce the number of variables, the quantity a - x is replaced by its value from Eq. (3.19). The result is

$$dc_{\rm B} = k_1 a e^{-(k_1 + k_2) t} dt$$

Integration yields

$$c_{\rm B} = -a \frac{k_1}{k_1 + k_2} e^{-(k_1 + k_2)t} + \text{const}$$

When determining the integration constant from the initial conditions  $c_B = 0$  at t = 0, we write an expression for the time dependence of the concentration of one of the products:

$$c_{\rm B} = a \frac{k_1}{k_1 + k_2} \left[ 1 - e^{-(k_1 + k_2)t} \right]$$
 (3.21)

An analogous expression with  $k_2$  being substituted for  $k_1$  is also obtained for the concentration  $c_{\rm C}$ :

$$c_{\rm C} = a \, \frac{k_2}{k_1 + k_2} \left[ 1 - e^{-(k_1 + k_2) \, t} \right] \tag{3.22}$$

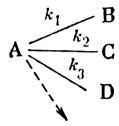
Dividing Eq. (3.21) by Eq. (3.22), we get the relation

$$\frac{c_{\rm B}}{c_{\rm C}} = \frac{k_1}{k_2}$$

which shows that during the entire course of the reaction and also at the end of it the ratio of the concentrations of the products

remains constant and equal to the ratio of the rate constants. Thus, having determined the relative amounts of the substances B and C at the end of reaction, we can, with the sum  $k_1 + k_2$  known, find also the individual values of the constants.

It is easy to see that with three or more parallel first-order reactions the result obtained will be similar to Eq. (3.18). Thus, if the reaction is written as



the integrated formula will look like

$$\ln \frac{a}{a-x} = (k_1 + k_2 + k_3) t$$

The concentrations (or amounts) of the products (provided that the original mixture does not contain them) will interrelate as constants, i.e.,

$$c_{\rm B}: c_{\rm C}: c_{\rm D}: \ldots = k_1: k_2: k_3: \ldots$$

For instance, the nitration of phenol involves three parallel firstorder (with respect to phenol) reactions, namely, the simultaneous formation of *ortho-*, *meta*, and *para-*nitrophenols. As shown by experiment, the ratio of the amounts of the three isomers remains constant during the course of the experiment:

$$c_o: c_m: c_p = 59.2: 3.3: 37.5 = k_o: k_m: k_p$$

Evidently, the *ortho*-isomer is formed with the highest velocity, and the *meta*-isomer with the lowest velocity.

## 3.3. Consecutive or Sequential Reactions

Of great importance in kinetics are consecutive reactions (or sequential reactions) which proceed from reactants to products not directly but through one or more intermediate stages at which more or less unstable intermediates are formed. It will not be an exaggeration to say that the majority of chemical reactions proceed through a number of consecutive steps, by one or the other mechanism. Intermediates may consist of ordinary molecules which become then involved in the reaction. In other cases, intermediates are free atoms or radicals exhibiting enhanced chemical activity as compared with bond-saturated molecules. An example

of a reaction proceeding by the free-radical mechanism is the oxidation of hydrogen to give water. A study of the kinetics of consecutive reactions constitutes a very important task. An exact mathematical solution of the equations derived for sequential reactions with the use of the basic kinetic law is however expedient only in the simplest cases. In more complicated cases, the solution of equations, if possible at all, leads to such unwieldy formulas that their practical utilization is at best very difficult.

Here we shall consider the rigorous solution of only one of the simplest cases, namely, the case of two consecutive first-order one-way reactions:

$$A \longrightarrow B \longrightarrow C$$

To the category of such reactions belongs, for example, the hydrolysis of esters of dicarboxylic acids. Thus, diethylmalonic ester is hydrolysed in two stages:

(I) 
$$CH_2$$
  $+ H_2O$   $\longrightarrow$   $CH_2$   $+ C_2H_5OH$   $COOC_2H_5$   $COOH$  (II)  $CH_2$   $+ H_2O$   $\longrightarrow$   $CH_2$   $+ C_2H_5OH$   $COOC_2H_5$   $COOH$   $COOC_2H_5$   $COOH$ 

Thus,

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C$$
ction  $(t = 0)$  the concentration

At the start of the reaction (t = 0) the concentration of A is a, the substances B and C being absent. By time t the concentrations are: a - x for the substance A; x - y for the substance B; and y for the substance C.

Applying the basic law of kinetics and the principle of independency, we obtain a system of differential equations:

(1) 
$$\frac{dx}{dt} = k_1 (a - x)$$
 (3.23)

(2) 
$$\frac{dy}{dt} = k_2 (x - y)$$
 (3 24)

The solution of the first equation, i.e., the simplest first-order equation, is represented in the form:

$$x = a \left( 1 - e^{-k_1 t} \right) \tag{3.25}$$

Substituting the values of x from Eq. (3.25) into Eq. (3.24) yields an equation for the rate of change of y:

$$\frac{dy}{dt} = -k_2 y + k_2 a \left(1 - e^{-k_1 t}\right) \tag{3.26}$$

This equation of the Leibnitz equation type is solved by equating provisionally the second term on the right-hand side of Eq. (3.26) to zero:

$$\frac{dy}{dt} = -k_2y$$

or

$$\ln y = -k_2 t + \ln z \tag{3.27}$$

where  $\ln z$  is the integration constant. Presenting Eq. (3.27) as

$$y = ze^{-k_2 t} \tag{3.28}$$

we take into account that z is not a true constant. It must be a function of time because of Eq. (3.26) being simplified. Further, to obtain the form of this function, we differentiate Eq. (3.28) with respect to time. We have:

$$\frac{dy}{dt} = \frac{dz}{dt} e^{-k_2 t} - z k_2 e^{-kt}$$

or, taking cognizance of Eq. (3.28),

$$\frac{dy}{dt} = -k_2 y + \frac{dz}{dt} e^{-k_2 t} \tag{3.29}$$

Now, comparing Eq. (3.29) with Eq. (3.26), we find that

$$dz = k_2 a \left[ e^{k_2 t} - e^{(k_2 - k_1) t} \right] dt$$

On integration this leads to

$$z = k_2 a \left[ \frac{1}{k_2} e^{k_2 t} + \frac{1}{k_2 - k_1} e^{(k_2 - k_1) t} \right] + \text{constant}$$
 (3.30)

Substituting the value of z into the expression for y, Eq. (3.28), gives:

$$y = k_2 a \left[ \frac{1}{k_2} - \frac{1}{k_2 - k_1} e^{-k_1 t} \right] + \text{const} \cdot e^{-k_2 t}$$
 (3.31)

The integration constant is found, as always, from the initial condition t = 0, y = 0:

$$const = a \frac{k_1}{k_2 - k_1}$$

Thus, we obtain the following expression for the dependence of the product concentration on time:

$$y = a \left( 1 + \frac{k_1}{k_2 - k_1} e^{-k_2 t} - \frac{k_2}{k_2 - k_1} e^{-k_1 t} \right)$$
 (3.32)

which will be treated in more detail at a later time.

For the present, we are to be certain that y = 0 at t = 0 and  $y \to a$  at  $t \to \infty$ , i.e., that the starting material will be entirely converted into the final product. Let us consider the intermediate

formed during the reaction. Subtracting Eq. (3.32) from Eq. (3.25), we have

$$x - y = a \frac{k_1}{k_2 - k_1} \left( e^{-k_1 t} - e^{-k_2 t} \right) \tag{3.33}$$

First consider a special case of this equation, where

$$k_1 = k_2 = k \tag{3.34}$$

Upon substitution of this equality Eq. (3.33) turns into an indeterminate form, which can be evaluated by using the ratio of the derived functions for  $k_1$ :

$$a \left[ \frac{e^{-k_1 t} - e^{-k_2 t} - k_1 t e^{-k_1 t}}{-1} \right]$$

Substitution of the values of  $k = k_1 = k_2$  gives a simple formula for the concentration of the reaction intermediate:

$$x - y = akte^{-kt} (3.35)$$

It is quite clear from relation (3.35) that x-y passes through a maximum—at small t the exponential is close to unity and the concentration of the intermediate increases almost in proportion to time, and with long reaction times there prevails the exponential function that tends to zero. As can easily be found by ordinary means, the time of attainment of the maximum concentration in this simple case is inversely proportional to the rate constant:

$$t_{\max} = \frac{1}{k}$$

The general expression (3.33) is of great interest. Here the function also has a maximum, which can easily be seen if we substitute the values of t=0 and  $t=\infty$ . In both cases, x-y vanishes, but at transient times the concentration of the intermediate is different from zero. The time of attainment of the maximum is found easily: it is determined by the values of the rate constants:

$$t_{\text{max}} = \frac{\ln \frac{k_2}{k_1}}{k_2 - k_1} \tag{3.36}$$

Now we find the maximum concentration by substituting (3.36) into (3.33):

$$(x-y)_{\max} = a \frac{k_1}{k_2 - k_1} \left( e^{-k_1 \frac{\ln \frac{k_2}{k_1}}{k_2 - k_1}} - e^{-\frac{k_2 \ln \frac{k_2}{k_1}}{k_2 - k_1}} \right)$$

Introducing a new variable

$$q = \frac{k_2}{k_1}$$

we see that the maximum concentration is independent of the separate values of the constants and is a function of their ratio:

$$(x-y)_{\text{max}} = \frac{a}{q-1} \left( e^{-\frac{\ln q}{q-1}} - e^{-\frac{q \ln q}{q-1}} \right)$$

or

$$(x-y)_{\max} = \frac{a}{q-1} \left( q^{-\frac{1}{q-1}} - q^{-\frac{q}{q-1}} \right)$$
 (3.37)

Now it is interesting to consider formula (3.37) at two limiting values of q.

1. The value of q is very small, i.e.,  $k_1 \bowtie k_2$ . This means that the intermediate B is relatively stable. If the low value of q is disregarded as compared with unity, Eq. (3.37) will assume the form:

$$(x-y)_{\text{max}} = \frac{a}{-1} (q^{+1} - q^{-q}) \approx a$$

that is, in this case the entire (almost!) amount of the reactant accumulates as an intermediate. The result obtained is trivial and it might have been expected since in the limit it corresponds to the complete absence of the second reaction  $(k_2 = 0)$ .

2. Suppose the intermediate is extremely unstable, i.e.,  $k_2 \gg k_1$  and q is very great. Then, in Eq. (3.37) unity may now be neglected as compared with q and

$$(x-y)_{\max} = \frac{a}{q} \left( q^{-\frac{1}{q}} - q^{-1} \right) \approx \frac{a}{q}$$

Since by condition q is great, the maximum concentration of the intermediate in this case is very low. The role of such particles, which are extremely unstable during the interaction with other molecules, can be played by atoms and free radicals.

Now let us turn to the final product C. The curve corresponding to the function y = f(t), (3.32), has an S-shaped form. It is not difficult to show that the second derivative  $d^2y/dt^2$  is equal to zero at  $t = t_{\text{max}}$ , i.e.,

$$\frac{d^2y}{dt^2} = 0 \quad \text{at} \quad t_{\inf} = \frac{\ln\frac{k_2}{k_1}}{k_2 - k_1} = t_{\max}$$
 (3.38)

In other words, the function y = f(t) has an inflection point and the time corresponding to this point coincides with the time of attainment of the maximum concentration of the reaction intermediate [see Eq. (3.36)]. The S-shape of the curve (Fig. 3.1) implies that the accumulation of the final product occurs as if with acceleration. First its concentration increases slowly and

then faster and faster and after the point of inflection is passed, its increase is slowed down. At the start of the reaction the amount of the end product formed may be too small to be detected analytically, and then, as if on a sudden, it begins to appear. This time interval elapsed before an appreciable amount of reaction has occurred, i.e., before the onset of the reaction is detected, is called the **induction period**  $(\tau)$ . The length of the induction period is undoubtedly associated with the accuracy of the analytical method employed.

Generally speaking, induction periods may arise from different factors. Here its presence is associated with the consecutive reaction. This concept will be encountered later in the discussion of

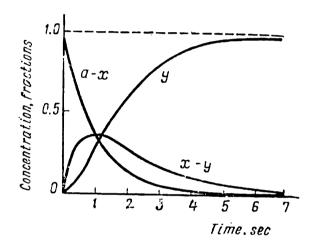


Fig. 3.1. The variation of the concentrations of the reactants for two consecutive first-order reactions:

(a-x)—reactant; (x-y)—intermediate; y—end product.

the kinetics of branched chain processes and autocatalytic reactions.

Let us return to the intermediate B. The height of the maximum of x - y, as has already been said, is determined by the ratio of the constants,  $k_2/k_1 = q$ . The higher the value of q, the lower the value of  $(x - y)_{\text{max}}$ . On the other hand, the time required for the maximum to be attained

$$t_{\text{max}} = \frac{\ln \frac{k_2}{k_1}}{k_2 - k_1}$$

also depends on the values of the constants. It can easily be seen that the larger the value of  $k_2$  at a given constant  $k_1$ , the more rapidly the maximum concentration can be attained.

Figure 3.2 gives three curves showing changes in the concentration of the intermediate when the latter is relatively unstable—its decomposition constant  $k_2$  exceeds by 10 times the formation constant  $k_1$ . The height of the maximum is the same in all the cases, but the shape of the curve is different since the time of attainment of the maximum depends also on the difference between the constants according to Eq. (3.36). Of special interest is curve 3 which shows that the decrease of the difference  $k_2 - k_1$  with their ratio being the same leads to the spreading of the maximum in time. The concentration of the intermediate continues to be approximately at a single low level close to the maximum for a long time. Thus, there is ground for stating that with the lapse of a certain short time period after the reaction has started (if  $k_2 \gg k_1$ ) there is established a nearly steady-state or sta-

tionary (quasi-stationary) concentration of the unstable intermediate, which persists for most of the reaction time. In the stationary state, the rate of formation of the reaction intermediate is nearly equal to its rate of disappearance. Therefore, the overall rate of change of its concentration, i.e., d(x-y)/dt, is equal to zero, more precisely, is considered to be equal to zero, not only at the point of the maximum but also for a relatively long time interval. What has been said above may be regarded as a substantiation of a very important, though approximate, method of kinetic treatment of complex reactions—the stationary- or steady-state principle, which is often associated with the name of Bodenstein (see Sec. 3.5).

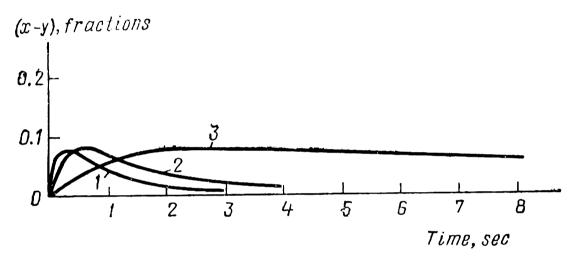


Fig. 3.2. The variation of the concentrations of the intermediate at the ratio of the constants  $k_2/k_1 = 10$ :

$$1-k_1=1$$
,  $k_2=10 \text{ sec}^{-1}$ ;  $2-k_1=0.5$ ,  $k_2=5 \text{ sec}^{-1}$ ;  $3-k_1=0.1$ ,  $k_2=1 \text{ sec}^{-1}$ .

The following considerations are also of interest. If the reaction intermediate is relatively unstable and  $k_2 > k_1$ , then, with the lapse of a sufficiently long period of time, the term  $\exp(-k_1t)$  will become much greater than  $\exp(-k_2t)$ . Equation (3.33) therefore reduces to the following:

$$x - y = a \, \frac{k_1}{k_2 - k_1} \, e^{-k_1 t}$$

If we divide the last equation by the time dependence of the amount of the starting substance, a - x, the following relation will obtain:

$$\frac{[B]}{[A]} = \frac{x - y}{a - x} = \frac{k_1}{k_2 - k_1}$$

which expresses the constancy of the ratio of the concentrations of the intermediate and the reactant in the *stationary* state. Sometimes, this state is termed the **transient equilibrium**. Somewhat different results are obtained when  $k_1$  is not only lower than  $k_2$  but is very low in absolute magnitude, i.e.,  $k_1 \ll k_2$ . Then, the

quantity  $k_1$  in the last equation may be disregarded as compared with  $k_2$ . So, we get:

$$\frac{[B]}{[A]} = \frac{x - y}{a - x} = \frac{k_1}{k_2} = \frac{\tau_2}{\tau_1} = \frac{T_2}{T_1}$$

that is, in the stationary state the concentrations of the reaction intermediate and the starting substance will be interrelated as their average lifetimes or half-life periods. In such cases, one speaks sometimes of the **secular equilibrium**. As an example may be cited the relation between the concentrations (or amounts) of radium and radon being in a state of secular equilibrium. As has already been mentioned (Chapter 1), the rate constant for the decay of radium is  $k_1 = 1.38 \times 10^{-11}$  and that of radon is  $k_2 = 2.097 \times 10^{-6}$  sec<sup>-1</sup>. Hence, in the stationary state (secular equilibrium) radon and radium are present in the following ratio:

$$\frac{N_{\rm Rn}}{N_{\rm Ra}} = \frac{1.37 \times 10^{-11}}{2.1 \times 10^{-6}} = 6.5 \times 10^{-4}$$

#### 3.4. n Consecutive First-Order Reactions

The mathematical solution of the problem of n consecutive first-order reactions was given in a most general form by A. V. Rakovsky in 1907. He studied the system

$$M_1 \longrightarrow M_2 \longrightarrow M_3 \longrightarrow M_4 \longrightarrow \ldots \longrightarrow M_n \longrightarrow M_{n+1}$$

which involves n reversible reactions.

We shall not dwell here on the consideration of this general solution because of the relations obtained being unwieldy and also of their being of little practical value; we shall limit ourselves to a simpler discussion of *n irreversible* first-order reactions:

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C \xrightarrow{k_3} D \xrightarrow{k_4} \dots$$

Let the number of molecules of the reactants at time t be  $N_1$  for substance A and  $N_2$  for B, etc. The initial (t = 0) number of molecules of A is equal to  $N_0$ . For substance A, we have evidently [see Eq. (2.8)]:

$$N_1 = N_0 e^{-k_1 t}$$

As known, for two reactions

$$A \longrightarrow B \longrightarrow C$$

we have

$$N_2 = N_0 \frac{k_1}{k_2 - k_1} \left( e^{-k_1 t} - e^{-k_2 t} \right)$$

that is, an expression identical with Eq. (3.33),

If the sequence consists of three reactions:

$$A \longrightarrow B \longrightarrow C \longrightarrow D$$

a third differential equation has to be added:

$$\frac{dN_3}{dt} = k_2N_2 - k_3N_3$$

Replacing  $N_2$  here by its expression from Eq. (3.33) and transposing  $k_3N_3$  to the left-hand side of the equality, we obtain:

$$\frac{dN_3}{dt} + k_3N_3 = N_0 \frac{k_1k_2}{k_2 - k_1} \left( e^{-k_1t} - e^{-k_2t} \right)$$

The solution of this equation has the form:

$$N_3 = N_0 \left( c_1 e^{-k_1 t} + c_2 e^{-k_2 t} + c_3 e^{-k_1 t} \right)$$

with the constants having the following values:

$$c_1 = \frac{k_1 k_2}{(k_2 - k_1) (k_3 - k_1)}, \quad c_2 = \frac{k_1 k_2}{(k_1 - k_2) (k_3 - k_2)}$$
  
and  $c_3 = \frac{k_1 k_2}{(k_1 - k_3) (k_2 - k_3)}$ 

In a general case, for n reactions the time dependence of the amount of the nth product is expressed by the following relation:

$$N_n = N_0 \left( c_1 e^{-k_1 t} + c_2 e^{-k_2 t} + \dots + c_n e^{-k_n t} \right)$$

where the constants are related to the rate constants as follows:

$$c_{1} = \frac{k_{1}k_{2}k_{3} \dots k_{n-1}}{(k_{2} - k_{1}) (k_{3} - k_{1}) (k_{4} - k_{1}) \dots (k_{n} - k_{1})}$$

$$c_{2} = \frac{k_{1}k_{2}k_{3} \dots k_{n-1}}{(k_{1} - k_{2}) (k_{3} - k_{2}) (k_{4} - k_{2}) \dots (k_{n} - k_{2})}$$

and so on.

The relationships that have been considered here are most important for the study of the kinetics of consecutive transformations of radioactive substances, where all the processes are undoubtedly of first order.

### 3.5. Two Consecutive Second-Order Reactions

Let us now examine a somewhat more complicated case, namely, one involving two consecutive second-order reactions:

$$2A \xrightarrow{k_1} 2A_1 \xrightarrow{k_2} A_2$$

Now we introduce the notation: a is the initial amount of substance A (moles) or the concentration in moles/litre; (a - x) is the amount of substance A by time t; (x - 2y) is the amount of

substance  $A_1$  by time t; y is the amount of substance  $A_2$  by time t; the initial simultaneous differential equations may be written as follows:

$$\frac{dx}{dt} = 2k_1 (a - x)^2 (3.39)$$

$$\frac{dy}{dt} = k_2 (x - 2y)^2 \tag{3.40}$$

The solution of Eq. (3.39) may be formulated thus:

$$x = \frac{abt}{1 + bt} \tag{3.41}$$

where  $b = 2k_1a$ . Further, passing over to Eq. (3.40) and replacing (x - 2y) by U, we get the following expression:

$$\frac{1}{2} \cdot \frac{d}{dt} \left( \frac{abt}{1+bt} - U \right) = k_2 U^2 \tag{3.42}$$

Equation (3.42) is of the type of Riccati equations. To solve this equation, one has first to select a partial solution and then, with the aid of this solution, the Riccati equation may be transformed into Bernoulli's equation. Let us seek a partial solution of Eq. (3.42) in the form:

$$U = \frac{n}{1 + bt}$$

It turns out that Eq. (3.42) has two partial solutions:

$$U_1 = \frac{n_1}{1+bt}, \qquad U_2 = \frac{n_2}{1+bt}$$
 (3.43)

where  $n_1$  and  $n_2$  are the roots of the quadratic equation

$$2k_2n^2 - bn - ab = 0 (3.44)$$

Namely,

$$n_1 = \frac{b}{4k_2} + \sqrt{\frac{b^2}{16k_2^2} + \frac{ab}{2k_2}}, \quad n_2 = \frac{b}{4k_2} - \sqrt{\frac{b^2}{16k_2^2} + \frac{ab}{2k_2}}$$

It is however obvious that  $U_2$  is negative \* and, hence, has no physical meaning. Using the partial solution of  $U_1$ , we can find the general solution of Eq. (3.42):

$$U = \frac{n_1}{1 + bt} + \theta {(3.45)}$$

<sup>\*</sup> In the solution proposed by A. D. Stepukhovich and L. M. Timonin (*Zhurn. Fiz. Khim.*, 25, 134, 1951) use is made of both partial solutions, i. e., the positive and the negative solution, the latter having no physical meaning. The final result for y, x-2y and  $t_0$  obtained in their work differs from the solution given here, which has been performed by V. L. Syaduk and V. M. Belova (at the Chemistry Department of the Moscow State University).

where 0 is a new, unknown function. Now Eq. (3.42) may be written in the following form:

$$\frac{d}{dt} \left( \frac{abt - n_1}{1 + bt} - \theta \right) = 2k_2 \left[ \frac{n_1^2}{(1 + bt)^2} + \frac{2n_1\theta}{1 + bt} + \theta^2 \right]$$
(3.46)

Differentiating the left-hand side of the equation, we obtain:

$$\frac{ab + bn_1}{(1+bt)^2} - \frac{d\theta}{dt} = 2k_2 \frac{n_1^2}{(1+bt)^2} + \frac{4k_2\theta n_1}{(1+bt)} + 2k_2\theta^2$$

Then, taking account of Eq. (3.44), we reduce the equation to the type of Bernoulli's equation:

$$\frac{d\theta}{dt} + \frac{4k_2n_1\theta}{1+bt} + 2k_2\theta^2 = 0$$

Now the substitution z = 1/0 is performed in this equation:

$$-\frac{dz}{dt}(1+bt)+4k_2n_1z+2k_2(1+bt)=0 (3.47)$$

Equation (3.47) is solved by equating provisionally the expression  $2k_2(1+bt)$  to zero and finding the time dependence of the intermediate integration constant. The resulting solution has the form:

$$z = 2k_2 (1 + bt) + \left(\frac{2k_2n_1 - b}{n_1}\right) (1 + bt)^{m-1}$$

where  $m = (4k_2n_1)/b$ . Substituting  $z = 1/\theta$ , we obtain the final solution for the amount of the reaction intermediate:

$$U = x - 2y = \frac{(b - 2k_2n_1)\left[1 - (1 + bt)^{m-1}\right]}{(1 + bt)\left[2k_2 - \frac{b - 2k_2n_1}{n_1}(1 + bt)^{m-1}\right]}$$
(3.48)

Now we are to find the extremal point of U = x - 2y, i. e., the maximum possible amount of the intermediate. To do this, we must find the derivative U and equate it to zero. As can be shown, dU/dt is equal to zero if the following condition is fulfilled:

$$F^2 - 8 \frac{k_2 n_1}{b} F + \frac{2k_2 n_1}{b - 2k_2 n_1} = 0 {(3.49)}$$

where

$$F = (1 + bt_0)^{m-1} (3.50)$$

Solving the quadratic equation (3.49) and employing expression (3.44) we find F, leaving only the positive value of the root since the negative value has no physical meaning:

$$F = \left(1 + \sqrt{1 + \frac{4}{r}}\right)\left(1 + \sqrt{1 + \frac{r}{4}}\right)$$

where

$$r = \frac{k_1}{k_2} \tag{3.51}$$

With account taken of the root  $n_1$  from Eq. (3.44), the exponent in Eq. (3.48) has the following value:

$$m - 1 = \sqrt{1 + \frac{4}{r}} \tag{3.52}$$

From Eqs. (3.50), (3.51), and (3.52) we find the time of attainment of the extremum:

$$t_0 = \frac{\left[\left(1 + \sqrt{1 + \frac{4}{r}}\right)\left(1 + \sqrt{1 + \frac{r}{4}}\right)\right]^{\frac{1}{\sqrt{1 + \frac{4}{r}}}} - 1}{2ak_1}$$
(3.53)

Substituting  $t_0$  into Eq. (3.48), we obtain an expression for the extremal value of the amount of the reaction intermediate:

$$U_{\text{(extremum)}} = x - 2y = \frac{2a\left[\left(1 + \sqrt{1 + \frac{4}{r}}\right)\right]}{\left[\left(1 + \sqrt{1 + \frac{4}{r}}\right)\left(1 + \sqrt{1 + \frac{r}{4}}\right)\right]} \times \frac{\left(1 + \sqrt{1 + \frac{r}{4}}\right)-1}{\left(1 + \sqrt{1 + \frac{4}{r}}\right)\left[\left(\sqrt{1 + \frac{4}{r}} - 1\right)\left(1 + \sqrt{1 + \frac{r}{4}}\right)\right]}$$
(3.54)

Examining Eq. (3.48) more thoroughly, we find first that the extremum corresponds to the maximum. Second, we become convinced that in limiting cases, i. e., for example, when  $k_2 \gg k_1$  (the reaction intermediate is extremely unstable) and  $r = k_1/k_2 \rightarrow 0$ ,  $(x-2y)_{\max} \rightarrow 0$ , i.e., the maximum concentration of the intermediate tends to zero. Otherwise  $(k_2 \ll k_1 \text{ and } r = k_1/k_2 \rightarrow 0)$  we have  $(x-2y)_{\max} \rightarrow a$ , i.e., all the initial substance accumulates as an intermediate.

Utilizing Eqs. (3.54) and (3.41), we arrive at an expression for the amount of the final product:

$$y = \frac{1}{2} \left\{ \frac{abt}{1+bt} - \frac{(b-2k_2n_1)\left[1-(1+bt)^{m-1}\right]}{(1+bt)\left[2k_2 - \frac{b-2k_2n_1}{n_1}(1+bt)^{m-1}\right]} \right\}$$
(3.55)

Analysis of this equation shows that the y = f(t) curve has a point of inflection; the time of attainment of this point,  $t_0$ , coincides

with the time of attainment of the maximum of the amount of the intermediate and is given by Eq. (3.53). That the point of inflection coincides with the maximum point in time can be shown with the aid of Eq. (3.40) by representing it in the form

$$y' = k_2 U^2$$

Further, we set the second derivative equal to zero:

$$y'' = 2k_2UU' = 0$$

From this it follows that the function y = f(t) has two points of inflection: (1) U = 0 at t = 0, i.e., at the origin of the coordinates. This means that the y = f(t) curve creeps, so to say, along the abscissa; (2) U' = 0 on the condition of (3.49), i.e.,

$$F^2 - \frac{8k_1n_1}{b}F + \frac{2k_2n_1}{b - 2k_1n_1} = 0$$

Hence, as a consequence, the coincidence of the time of attainment of the maximum x-2y with the point of inflection on the curve of the amount of products versus time.

The equations considered in this section may find application in the study of isomerization processes in those cases where the overall rate of the reaction is controlled by the initial bimolecular second-order step.

### 3.6. The Steady-State Approximation and the Mechanism of Complex Gas Reactions

As shown in the preceding sections, an exact mathematical solution of the problem of two consecutive reactions leads to formulas which are inconvenient for practical utilization. Thus, the equations obtained for the concentrations of the final product and the intermediate cannot be solved for the constants. Hence, the constants can no longer be calculated directly from experimental data on the concentration-time relationship. They have to be selected. We can imagine to what extent the equations will become unwieldy in more complex cases, for example, for several consecutive and parallel reactions of different orders. And it is such a set of processes that constitute the mechanisms of many ordinary reactions, such as the formation of hydrogen bromide or water. An exact mathematical solution of the problem often proves to be impossible, in which case resort is made to the approximation steady-state method (the steady-state approximation)\* in kinetic studies. In addition to what has been said earlier (page 69), we give a more rigorous substantiation of the method.

<sup>\*</sup> This method is also known as the Bodenstein steady-state approximation, the steady- (or stationary-) state principle, or the steady-state hypothesis, — Tr.

Let us consider the reaction

$$A + B \longrightarrow 2C$$
 (A)

assuming that it proceeds by a mechanism involving two highly unstable products  $M_1$  and  $M_2$ , i. e.,

(1) 
$$\Lambda \longrightarrow 2M_1$$
  $k_1$   
(2)  $M_1 + B \longrightarrow C + M_2$   $k_2$   
(3)  $M_2 + A \longrightarrow C + M_1$   $k_3$   
(4)  $M_1 + M_1 \longrightarrow A$   $k_4$ 

The first of these elementary reactions is unimolecular and the remaining ones are bimolecular. First we will write down the rates of change of the concentrations of the stable substances:

$$-\frac{d[A]}{dt} = k_1[A] + k_3[M_2][A] - k_4[M_1]^2$$

$$-\frac{d[B]}{dt} = k_2[M_1][B]$$

$$+\frac{d[C]}{dt} = k_2[M_1][B] + k_3[M_2][A]$$
(3.56)

and then the equations for the intermediates  $M_1$  and  $M_2$ :

$$\frac{d[M_1]}{dt} = 2k_1[A] - k_2[M_1][B] + k_3[M_2][A] - 2k_4[M_1]^2 
\frac{d[M_2]}{dt} = k_2[M_1][B] - k_3[M_2][A]$$
(3.57)

From the stoichiometric equations (A) and (B) we can also deduce the number of moles that have reacted \*:

$$[A]_{0} - [A] = \frac{[C]}{2} + \frac{[M_{1}]}{2}$$

$$[B]_{0} - [B] = \frac{[C]}{2} + [M_{2}]$$
(3.58)

In accordance with what has been said in Sec. 3.3, the concentrations of the unstable intermediates,  $[M_1]$  and  $[M_2]$ , are very small during the entire reaction as compared with the concentrations of the reactants and stable products. In this connection, the stoichiometric relations (3.58) can be simplified:

$$[A]_0 - [A] = \frac{[C]}{2}$$
 and  $[B]_0 - [B] = \frac{[C]}{2}$  (3.59)

Differentiation of the above relations with respect to time gives the expressions

$$-\frac{d[A]}{dt} = \frac{1}{2} \cdot \frac{d[C]}{dt} \quad \text{and} \quad -\frac{d[B]}{dt} = \frac{1}{2} \cdot \frac{d[C]}{dt}$$
 (3.60)

<sup>\*</sup> The volume of the reacting system is assumed to be constant.

which shows the absence of an appreciable lag of the rate of accumulation of the products behind the rate of disappearance of the reactants.

We may substitute the expression for the rates from Eq. (3.56) into Eq. (3.60). We thus obtain:

$$-\frac{d[A]}{dt} = \frac{1}{2} \cdot \frac{d[C]}{dt} = k_1[A] + k_3[M_2][A] - k_4[M_1]^2 =$$

$$= \frac{1}{2} k_2[M_1][B] + \frac{1}{2} k_3[M_2][A]$$

or

$$2k_1[A] - k_2[M_1][B] + k_3[M_2][A] - 2k_4[M_1]^2 = 0$$

But, according to Eq. (3.57), the last expression is equal to  $d[M_1]/dt$ . Hence,

$$\frac{d\left[\mathsf{M}_{1}\right]}{dt} = 0\tag{3.61}$$

Analogously, using the second of Eqs. (3.60), we obtain:

$$-\frac{d[B]}{dt} = \frac{1}{2} \cdot \frac{d[C]}{dt} = k_2[M_1][B] = \frac{1}{2}[M_1][B] + \frac{1}{2}k_3[M_2][A]$$

or

$$k_2[M_1][B] - k_3[M_2][A] = 0$$

That is, according to Eq. (3.57),

$$\frac{d\left[M_2\right]}{dt} = 0\tag{3.62}$$

Thus, as a result of the formation of unstable intermediates in very small concentrations, the important steady-state conditions (3.61) and (3.62) are obtained.

The practical importance of the steady-stale principle is very great. By setting the overall rates of formation-decomposition of the unstable intermediates to zero, the steady-state approximation enables their concentrations to be expressed in terms of the concentrations of readily analysable substances and then to substitute them into the rate equation for the reaction under study. This equation is compared with the empirical rate equation and the suitability of the supposed reaction mechanism is thus decided.

Let us consider the use of the steady-state approximation on some examples. We shall begin with the Butlerov reaction (1867) which is the simultaneous decomposition of hydrogen iodide and alkyl iodide:

$$RI + HI \longrightarrow RH + I_2$$

This reaction is, so to say, an analogue of the well-known reaction of decomposition of pure hydrogen iodide:

$$HI + HI \longrightarrow H_2 + I_2$$

which is of second order (see Sec. 3.1).

It was originally believed that the Butlerov reaction too had an ordinary persistent second order, at least within a single experiment, i.e., at one value of the initial concentration of HI; the second-order rate constant from the equation

$$\frac{d\left[I_2\right]}{dt} = k_{II}\left[RI\right]\left[HI\right] \tag{3.63}$$

exhibits good constancy. However, the subsequent investigations carried out by Ogg in 1934 showed the dependence of  $k_{\rm II}$  in Eq. (3.63) on the initial concentration of HI, which obviously must not be the case with a normal second-order reaction. It was found exactly that  $k_{\rm II}$  diminishes with increasing initial concentration of hydrogen iodide:

$$k_{\rm II} = k' + \frac{k''}{[\rm HI]_0}$$

In other words, the differential equation for the rate of the Butlerov reaction must on the whole be written down, according to experiment, as follows:

$$\frac{d\left[I_{2}\right]}{dt} = \left\{k' + \frac{k''}{|HI|_{0}}\right\} [RI][HI] \tag{3.64}$$

But how could one explain this seeming violation of the basic law of chemical kinetics, which manifests itself as the dependence of the "constant" on the concentration? According to Ogg, the phenomenon is accounted for by the assumption of the complicated mechanism of the Butlerov reaction. To put it more exactly, according to the assumption, the reaction proceeds by two mechanisms. The first mechanism is an ordinary bimolecular second-order reaction:

I. (1) 
$$RI + HI \longrightarrow RH + I_2$$
  $k_1$ 

The second mechanism is complicated: it consists of four elementary, consecutive and parallel reactions involving atoms and free radicals:

II. (2) RI 
$$\longrightarrow$$
 R + I slow  $k_2$   
(3) R + HI  $\longrightarrow$  RH +  $l$  fast  $k_3$   
(4) R + I<sub>2</sub>  $\longrightarrow$  RI + I fast  $k_4$   
(5) I + I + M  $\longrightarrow$  I<sub>2</sub> + M fast  $k_5$ 

Here it is assumed that reaction 2 involving the breakdown of the molecule RI into a free radical R and an iodine atom, which requires the consumption of a considerable amount of energy, proceeds slowly. All the other reactions, which involve free atoms or radicals, occur with relatively high velocities.

The consecutive reactions that constitute the second mechanism give rise to two highly reactive and, hence, unstable intermediates R and I, for which the rates of formation are much lower than their rates of disappearance. In the notation adopted in the description of the kinetics of consecutive reactions [formula (3.37)], this corresponds to large values of q. In other words, the intermediates R and I accumulate in very small concentrations. Hence, the steady-state principle may be applied to these intermediates, i.e., it may be assumed that

$$\frac{d[R]}{dt} = 0 \quad \text{and} \quad \frac{d[I]}{dt} = 0$$

Proceeding from the basic kinetic law and the principle of independency, we may write the overall rate of formation-disappearance of iodine atoms:

$$\frac{d[I]}{dt} = k_2[RI] + k_3[R][HI] + k_1[R][I_2] - 2k_5[I]^2[M] = 0$$
 (3.65)

Analogously, for the overall rate of change of the concentration of the radical R we obtain:

$$\frac{d[R]}{dt} = k_2[RI] - k_3[R][HI] - k_4[R][I_2] = 0$$
 (3.66)

Adding together expressions (3.65) and (3.66), we get:

$$k_2 [RI] = k_5 [I]^2 [M]$$
 (3.67)

Using this equation, we can easily determine the concentration of iodine atoms.

Equation (3.66) is readily solved for the concentration of free radicals:

$$[R] = \frac{k_2 [RI]}{k_3 [HI] + k_4 [I_2]}$$
 (3.68)

Thus, the steady-state method allows one to express the concentrations of unstable intermediates in terms of the concentrations of ordinary, relatively stable and, hence, readily analytically determinable substances. In this lies, generally speaking, the fundamental significance of the application of the steady-state principle.

Now let us determine the overall observed rate of the Butlerov reaction from the appearance of molecular iodine and write the

equation

$$\frac{d[I_2]}{dt} = k_1[RI][HI] - k_4[R][I_2] + k_5[I]^2[M]$$
 (3.69)

Replacing the concentration [R] here by its value from expression (3.68) and using, instead of the last term, the product  $k_2$  [RI] equal to it, (3.67), we get

$$\frac{d [I_2]}{dt} = k_1 [RI] [III] - \frac{k_2 k_4 [RI] [I_2]}{k_3 [HI] + k_4 [I_2]} + k_2 [RI] = 
= k_1 [RI] [HI] + \frac{k_2 k_3 [RI] [HI]}{k_3 [HI] + k_4 [I_2]}$$
(3.70)

Then, on the basis of the likely assumption of the closeness of the rates of similar reactions (3) and (4), i.e., of the equality

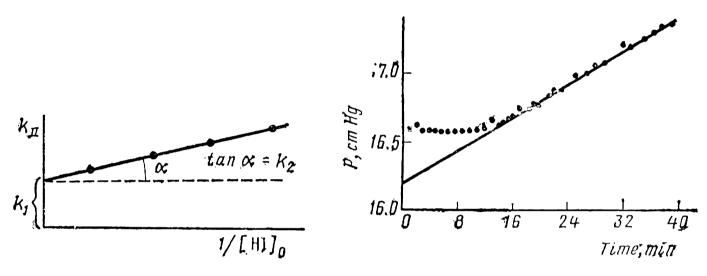


Fig. 3.3. The rate constant of the Butlerov reaction versus the initial concentration of hydrogen iodide.

Fig. 3.4. The variation of pressure in the reaction vessel during the thermal decomposition of methane (according to the data obtained by Kassel, 1932).

 $k_3 = k_4$ , these constants cancel out in expression (3.70). If, finally, we take into account the constancy of the sum of the concentrations [HI] and [I<sub>2</sub>], which is equal to the initial concentration of hydrogen iodide [HI]<sub>0</sub>, we will finally obtain:

$$\frac{d[I_2]}{dt} = \left\{ k_1 + \frac{k_2}{[HI]_0} \right\} [RI][I_2]$$
 (3.71)

What remains now is to compare the theoretical expression (3.71) with the experimentally found equation (3.64) and to check out whether they are functionally identical. Thus, the Ogg mechanism of the Butlerov reaction and its treatment by means of the steady-state principle enables one to account for the experimentally established dependence of the second-order rate constant on the initial concentration of hydrogen iodide. Graphically this dependence may be represented by a straight line in the coordinates  $k_{\rm II}$  and  $1/[{\rm HI}]_0$  (Fig. 3.3).

The Kinetics of Thermal Decomposition of Methane. Applying the manometric method of measuring reaction rates, Kassel (1932) studied the kinetics of the thermal decomposition of methane in a static system in a temperature range of 735-1113 °C.

The typical course of the change of pressure in Kassel experi-

ments is shown in Fig. 3.4.

At the very beginning of the reaction there was often observed an induction period, following which the pressure in the reaction vessel increased linearly with time with the decomposition of methane being not too strong, which indicated that the reaction was first order. The first order was confirmed by experiments at different initial pressures. Below are presented the first-order rate constants found from the initial reaction rates at 735 °C from the straight-line portions of curves of the type shown in Fig. 3.4.

Initial pressure, cm Hg 1.3 2.44 2.60 4.75 11.18 16.47 29.64 
$$k \cdot 10^5$$
, sec<sup>-1</sup> 1.19 1.06 1.40 1.13 1.21 1.03 1.14

As has been found, the reaction is sharply retarded by hydrogen, in the presence of which the velocity is approximately defined by the equation

 $-\frac{d \left[ \text{CH}_1 \right]}{dt} = k \frac{\left[ \text{CH}_1 \right]^2}{\left[ \text{H}_2 \right]^3}$  (3.72)

To account for the observed specific features of the reaction kinetics, Kassel suggested the following mechanism:

$$CH_{4} \rightleftharpoons CH_{2} + H_{2} \qquad k_{1}, r_{1}$$

$$CH_{2} + CH_{4} \rightleftharpoons C_{2}H_{6} \qquad k_{2}, r_{2}$$

$$C_{2}H_{6} \rightleftharpoons C_{2}H_{4} + H_{2} \qquad k_{3}, r_{3}$$

$$C_{2}H_{4} \rightleftharpoons C_{2}H_{2} + H_{2} \qquad k_{4}, r_{4}$$

$$C_{2}H_{2} \rightleftharpoons 2C + H_{2} \qquad k_{5}, r_{5}$$

All the reactions listed were assumed to be reversible; the quantities  $k_i$  and  $r_i$  express the rate constants for the forward and reverse reactions. A specific feature of the proposed mechanism is the initial formation of the methylene radical,  $CH_2$  which then enters into reaction with methane to form ethane. From the latter, by way of removal of the hydrogen molecules, there are formed ethylene and acetylene, the latter being decomposed finally into carbon and hydrogen.

Kassel thought that the steady-state principle could be applied to the four expected intermediates  $(CH_2, C_2H_6, C_2H_4, \text{ and } C_2H_2)$ . Let us write the appropriate equations, introducing the following notations:  $[CH_4] = a$ ,  $[CH_2] = x$ ,  $[H_2] = b$ ,  $[C_2H_6] = y$ ,  $[C_2H_4] = z$ ,

and  $[C_2H_2] = \varphi$ :

I. 
$$\frac{d \left[ \text{CH}_2 \right]}{dt} = k_1 a - k_2 a x - r_1 b x + r_2 y = 0$$
II. 
$$\frac{d \left[ \text{C}_2 \text{H}_6 \right]}{dt} = k_2 a x - r_2 y - k_3 y + r_3 b z = 0$$
III. 
$$\frac{d \left[ \text{C}_2 \text{H}_4 \right]}{dt} = k_3 y - r_3 b z - k_4 z + r_4 b \phi = 0$$
IV. 
$$\frac{d \left[ \text{C}_2 \text{H}_4 \right]}{dt} = k_4 z - r_4 b \phi - k_5 \phi + r_5 b = 0$$

The task here, as always in such cases, consists in excluding the concentrations of unstable products so as to express eventually the directly observed rate of the reaction,  $-d [CH_4]/dt$ , as a function of the reactant and stable reaction products.

The task can be solved, for example, as follows. From Equations I and II we omit x and solve the result for y:

$$y = \frac{r_3 b z (k_2 a + r_1 b) + k_1 k_2 a^2}{r_1 b (r_2 + k_3) + k_2 k_3 a}$$
(3.73)

Then, solving Equation III for y, we obtain

$$y = \frac{r_3bz + k_4z - r_4b\phi}{k_2} \tag{3.74}$$

Equating Eqs. (3.73) and (3.74), we solve the resulting relation for z:

$$z = \frac{k_1 k_2 k_3 a^2 + r_4 b \varphi \left[ r_1 \left( r_2 + r_3 \right) b + k_2 k_3 a \right]}{r_1 r_2 r_3 b^2 + r_1 k_4 \left( r_2 + k_3 \right) b + k_2 k_3 k_4 a}$$
(3.75)

Now we find z from Equation IV:

$$z = \frac{r_4 b \phi + k_5 \phi - r_5 b}{k_4} \tag{3.76}$$

From Equations (3.75) and (3.76) we exclude z and determine  $\varphi$ :

$$\varphi = \frac{k_1 k_2 k_3 k_4 a^2 + k_2 k_3 k_4 r_3 a b + r_1 r_2 r_3 r_5 b^3 + r_1 r_2 r_5 k_4 b^2 + r_1 r_5 k_4 k_3 b^2}{k_2 k_3 k_4 k_5 a + r_1 r_2 r_3 r_4 b^3 + r_1 r_2 r_3 k_5 b^2 + r_1 r_2 k_4 k_5 b + r_1 k_3 k_4 k_5 b}$$

Passing over to the rate of the observed reaction, we take into account that all the reactions proceeding by the mechanism (3.75) are interconnected and, hence, the rate of decomposition of methane must be equal to the doubled rate of decomposition-formation of acetylene according to reaction (5), i.e.,

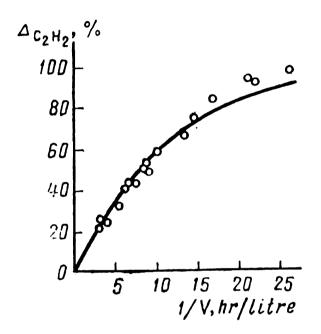
$$\frac{d \left[ \text{CH}_{i} \right]}{dt} = 2 \left\{ k_{5} \left[ \text{C}_{2}\text{H}_{2} \right] - r_{5} \left[ \text{H}_{2} \right] \right\} =$$

$$= 2 \frac{k_{1}k_{2}k_{3}k_{4}k_{5} \left[ \text{CH}_{4} \right]^{2} - r_{1}r_{2}r_{3}r_{4}r_{5} \left[ \text{H}_{2} \right]^{4}}{r_{1}r_{2}r_{3}r_{4} \left[ \text{H}_{2} \right]^{3} + r_{1}r_{2}r_{3}k_{5} \left[ \text{H}_{2} \right]^{2} + r_{1} \left( r_{2} + k_{3} \right) k_{4}k_{5} \left[ \text{H}_{2} \right] + k_{2}k_{3}k_{4}k_{5} \left[ \text{CH}_{4} \right]}$$
(3.77)

In the absence of hydrogen in the early stages of the reaction Eq. (3.77) assumes the following simple form:

$$-\frac{d\left[\text{CH}_4\right]}{dt} = 2k_1\left[\text{CH}_4\right]$$

that is, the reaction is first order, just as is observed experimentally, the appearance of the factor 2 being associated with the fact that the first reaction is followed by the second, faster reaction which also involves the methane molecule.



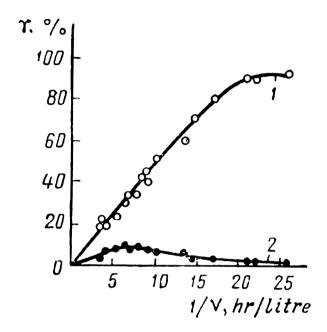


Fig. 3.5. The degree of conversion of acetylene versus the reaction time.

The unfilled circles on the calculated first-order curve are the experimental data.

Fig. 3.6. The degree of conversion of acetylene into solid products (1) and gaseous derivatives of acetylene (2) versus the reaction time.

Applying Eq. (3.77) to the equilibrium, we obtain the relation

$$\frac{k_1 k_2 k_3 k_4 k_5}{r_1 r_2 r_3 r_4 r_5} = \frac{[H_2]^4}{[CH_4]^2}$$

which may be regarded as the equilibrium constant for the formation of methane from its elements. Determining the numerical value of this constant by the thermodynamic method, the author arrives at the conclusion that under the conditions of his experiments at a temperature of  $760\,^{\circ}$ C, the re-formation of methane, which starts with the synthesis of acetylene, does not take place. Therefore, the constant  $r_5$  is small and all the terms containing it may be neglected. Besides, if the hydrogen concentration is considerable, we may neglect all the terms in the denominator, except the first one. Thus, in the presence of hydrogen

$$-\frac{d \left[ \text{CH}_4 \right]}{dt} = \frac{2k_1k_2k_3k_4k_5 \left[ \text{CH}_4 \right]^2}{r_1r_2r_3r_4 \left[ \text{H}_2 \right]^3} = k \frac{\left[ \text{CH}_4 \right]^2}{\left[ \text{H}_2 \right]^3}$$

The last equation indicates that the reaction is retarded by hydrogen. Functionally it coincides with the empirically found relation

between the reaction rate and the hydrogen concentration

[Eq. (3.72)].

Thus, the mechanism proposed by Kassel leads to kinetic equations that satisfy the empirical relationships. These coincidences should not be overestimated since, according to Kassel, the agreement between the mechanism and the observed kinetics does not yet prove the validity of the mechanism. The disagreement between the mechanism and the kinetics, however, proves, without doubt, its unsuitability.

Decomposition of Acetylene and Ethane in the Glow Discharge. The reactions were investigated by Borisova and Yeremin in 1965. The decomposition of acetylene to  $\Delta_{C_2H_2} \approx 70$  per cent obeys the first-order law (Fig. 3.5). The main reaction products are solid polymers and hydrogen; the gaseous derivatives of acetylene are formed in a considerably smaller amount (Fig. 3.6).

The authors proposed the mechanism of the reaction initiated by an electron impact:

(1) 
$$C_2H_2 + \stackrel{\leftarrow}{e} \longrightarrow C_2H + H + e$$
  $k_1$   
(2)  $C_2H_2 + H \longrightarrow C_2H + H_2$   $k_2$   
(3)  $C_2H + C_2H_2 \longrightarrow C_4H_3$   $k_3$   
(4)  $H \xrightarrow{\text{wall}} \frac{1}{2}H_2$   $k_4$ 

The polymerization begins with process 3. The radical  $C_4H_3$  formed in this process enters into reaction with one more acetylene molecule, etc.

The stationary-state principle is applied to the hydrogen atoms and the radical  $C_2H$ :

$$\frac{d \left[ C_2 H \right]}{dt} = k_1 \left[ C_2 H_2 \right] + k_2 \left[ C_2 H_2 \right] \left[ H \right] - k_3 \left[ C_2 H \right] \left[ C_2 H_2 \right] = 0$$

$$\frac{d \left[ H \right]}{dt} = k_1 \left[ C_2 H_2 \right] - k_2 \left[ C_2 H_2 \right] \left[ H \right] - k_4 \left[ H \right] = 0$$
(3.78)

When determining the concentrations of  $C_2H$  and H from these equations, we substitute them into the rate equation for the decomposition of acetylene:

$$-\frac{d\left[C_{2}H_{2}\right]}{dt} = k_{1}\left[C_{2}H_{2}\right] + k_{2}\left[C_{2}H_{2}\right]\left[H\right] + k_{3}\left[C_{2}H\right]\left[C_{2}H_{2}\right]$$
(3.79)

As a result, we obtain

$$-\frac{d\left[C_{2}H_{2}\right]}{dt} = 2k_{1}\left[C_{2}H_{2}\right]\left\{1 + \frac{k_{2}\left[C_{2}H_{2}\right]}{k_{2}\left[C_{2}H_{2}\right] + k_{4}}\right\}$$
(3.80)

Equation (3.80) simplifies if it is assumed that under the conditions of the hindered surface recombination of hydrogen atoms (reaction 4) the constant  $k_4$  is small as compared with the product

 $k_2$  [C<sub>2</sub>H<sub>4</sub>] and it may be neglected. Then

$$-\frac{d [C_2 H_2]}{dt} = 4k_1 [C_2 H_2]$$

and the reaction is described by a first-order equation according to experimental data. It is interesting that the overall rate of decomposition of acetylene is equal to the quadrupled rate of the primary act.

The same authors have investigated the kinetics of decomposition of ethane in the glow discharge. To account for the data obtained, the following mechanism has been suggested:

(1) 
$$C_2H_6 + e \longrightarrow 2CH_3 + e$$
  $k_1$   
(2)  $C_2H_6 + e \longrightarrow C_2H_5 + H + e$   $k_2$   
(3)  $C_2H_6 + H \longrightarrow C_2H_5 + H_2$   $k_3$   
(4)  $CH_3 + C_2H_6 \longrightarrow CH_4 + C_2H_5$   $k_4$   
(5)  $C_2H_5 + e \longrightarrow C_2H_4 + H + e$   $k_5$   
(6)  $C_2H_5 + e \longrightarrow C_2H_3 + H_2 + e$   $k_6$   
(7)  $C_2H_3 + e \longrightarrow C_2H_2 + H + e$   $k_7$   
(8)  $H \longrightarrow \frac{1}{2}H_2$   $k_8$ 

in which the main role is played by the activation of molecules and radicals by an electron impact, which is accompanied by the decomposition of the excited particles.

The treatment of the mechanism by means of the steady-state method gives the following simple expression for the rate of the decomposition of ethane:

$$-\frac{d\left[C_{2}H_{6}\right]}{dt} = (3k_{1} + k_{2})\left[C_{2}H_{6}\right] + 2k_{3}\frac{k_{1} + k_{2}}{k_{8}}\left[C_{2}H_{6}\right]^{2}$$

Thus, depending on the conditions, there may be observed both first-order and second-order reactions. For instance, at low temperatures in the glow discharge the constant  $k_3$  may be found to be small, in which case the reaction will be first order.

Synthesis of Ozone from a Mixture of Oxygen and Nitrogen. The synthesis of ozone in a barrier electrical discharge \* in an ozonizer is described by an empirical equation of the following type:

$$\frac{d [O_3]}{dt} = k_0 [O_2] - k_1 [O_3] \tag{3.81}$$

<sup>\*</sup> For reactions taking place in electrical discharges, see Chapter 11.

which seems to be an ordinary equation of a first-order reversible reaction. But, as has been shown by the investigations carried out by Filippov, the constant  $k_0$  appears to be peculiarly dependent on the mole fraction of nitrogen,  $\gamma_{N_2}$ , in the original mixture. This dependence means that the equilibrium-stationary concentration of ozone, which results with a long reaction time, passes through a maximum with increasing  $\gamma_{N_2}$ . The phenomenon has been accounted for by the activating effect of nitrogen. On the whole, the mechanism of formation-decomposition of ozone is described by a sequence of the following elementary processes:

$$(1) O_2 + \stackrel{\leftarrow}{e} \longrightarrow O + O + e \qquad \qquad k_1$$

$$(2) O + O_2 + M \longrightarrow O_3 + M \qquad \qquad k_2$$

$$(3) O_3 + M \longrightarrow O_2 + O + M \qquad \qquad k_3$$

$$(4) N_2 + \stackrel{\leftarrow}{e} \longrightarrow N_2^* + e \qquad \qquad k_4$$

$$(5) N_2^* + O_2 \longrightarrow N_2 + O + O \qquad \qquad k_5$$

$$(6) N_2^* + N_2 \longrightarrow N_2 + N_2 \qquad \qquad k_6$$

Processes 1 and 4 are collisions between the molecules and sufficiently fast electrons. In the first case, the  $O_2$  molecule dissociates into atoms, and in the second the nitrogen molecule passes into an excited state,  $N_2^*$ . The energy of excitation can be imparted to the oxygen molecule, which is thus dissociated (process 5), or it may be dissipated upon collision with another nitrogen molecule (process 6).

The stationary-state principle is applied to the oxygen atoms and the excited nitrogen molecules:

$$\frac{d[O]}{dt} = k_1[O_2] - k_2[O][O_2][M] + k_3[O_3][M] + k_5[N_2^*][O_2] = 0$$
 (3.82)

and

$$\frac{d\left[N_{2}^{*}\right]}{dt} = k_{4}\left[N_{2}\right] - k_{5}\left[N_{2}^{*}\right]\left[O_{2}\right] - k_{6}\left[N_{2}^{*}\right]\left[N_{2}\right] = 0$$
 (3.83)

In writing these equations it is assumed that the concentration of electrons, [e], is constant and may be included in the rate constant. Further, it is thought that the formation of oxygen atoms by reaction 3 is relatively insignificant and therefore the term  $k_3[O_3][M]$  may be ignored as compared with the other terms. Thus, from Eq. (3.82) there is obtained the steady-state concentration of oxygen atoms:

$$[O] = \frac{k_1}{k_2 [M]} + \frac{k_5 [N_2^*]}{k_2 [M]}$$
 (3.84)

and from Eq. (3.83) we obtain the steady-state concentration of excited nitrogen molecules:

$$[N_2^*] = \frac{k_4 [N_2]}{k_5 [O_2] + k_6 [N_2]}$$
(3.85)

The overall rate of formation-decomposition of ozone will be given, in accordance with the mechanism, by the equation \*

$$\frac{d [O_3]}{dt} = k_2 [O] [O_2] [M] - k_3 [O_3] [M]$$
 (3.86)

Substitution of Eqs. (3.84) and (3.85) into Eq. (3.86) yields

$$\frac{d [O_3]}{dt} = \left\{ k_1 + \frac{k_1 k_5 [N_2]}{k_6 [N_2] + k_5 [O_2]} \right\} [O_2] - k_3 [M] [O_3]$$
 (3.87)

This equation should be compared with the empirical equation (3.81). It then follows that the role of the constants in Eq. (3.87) is played by the quantities

 $k_0 = \left\{ k_1 + \frac{k_1 k_5 [N_2]}{k_6 [N_2] + k_5 [O_2]} \right\}$   $k_1 = k_3 [M]$ 

and

The result obtained is in agreement with the experimentally established dependence of the formation constant for ozone,  $k_0$ , on the composition of the mixture, and also with the fact that the decomposition constant  $k_1$  is independent of the composition.

Thermal Formation of Hydrogen Bromide. Of great interest is the reaction of formation of hydrogen bromide studied by Bodenstein and Lind (1906):

$$H_2 + Br_2$$
 (vapour)  $\longrightarrow$  2IIBr

The study was conducted at temperatures between 230 and 300 °C. These authors found that, in distinction to the externally similar reaction of formation of hydrogen iodide, in this case the kinetic equation has a rather complicated form. Namely,

$$\frac{d [HBr]}{dt} = k \frac{[H_2] [Br_2]^{1/2}}{1 + \frac{[HBr]}{10[Br_2]}}$$
(3.88)

The cause for this complexity of the equation remained unexplained until the period 1919-1920, when at about the same time and independently of one another, three scientists, namely, Christiansen, Herzfeld and Polanyi, suggested a mechanism explaining the complexity of Eq. (3.88). This mechanism allows for the

<sup>\*</sup> Reaction 3 is not taken into account for the formation of oxygen atoms but is necessarily included in the equation for ozone.

formation of free bromine and hydrogen atoms as intermediates. Namely,

(1) 
$$Br_2 \longrightarrow Br + Br$$
  $k_1$   
(2)  $Br + H_2 \longrightarrow HBr + H$   $k_2$   
(3)  $H + Br_2 \longrightarrow HBr + Br$   $k_3$   
(4)  $H + HBr \longrightarrow H_2 + Br$   $k_4$   
(5)  $Br + Br \longrightarrow Br_2$   $k_5$ 

From a modern standpoint, there is an inaccuracy in this mechanism: it allows for a bimolecular recombination of bromine atoms into a molecule (reaction 5). The requisite participation of a third particle M does not alter the form of the equation.

It is left to the reader to check out whether the application of the steady-state principle to the concentrations of free hydrogen and bromine atoms leads to an equation of the form (3.88).

It may be noted, in general, that the appearance in the kinetic equation of the concentration raised to a power of  $\frac{1}{2}$  usually indicates the participation in the reaction mechanism of free atoms or radicals which are destroyed predominantly as a result of the recombination upon collision between them. The rate of such a recombination, for example, reaction 5, in the mechanism under consideration is evidently proportional to the square of the concentration \*.

Rice and Herzfeld, who are the authors of the well-known mechanism of the pyrolytic decomposition of ethane \*\*, explained (1934) in a more general form why the observed rates in the complicated free-radical mechanism of decomposition of hydrocarbons are often described by first-order equations. As an example, they cited the decomposition of a hydrocarbon  $M_1$ , which

(1) 
$$C_2H_6 \longrightarrow 2CH_3$$

(2) 
$$CH_3 + C_2H_6 \longrightarrow CH_4 + C_2H_5$$

$$(4) H + C_2H_6 \longrightarrow H_2 + C_2H_5$$

(5) 
$$2H \longrightarrow H_2$$
 (a triple collision)

(6) 
$$H + C_2H_5 \longrightarrow C_2H_1 + H_2$$
  
or  $C_2H_6$ 

(7) 
$$H + CH_3 \longrightarrow CH_4$$

(8) 
$$CH_3 + C_2H_5 \longrightarrow C_3H_8$$

<sup>\*</sup> In my opinion, the use of the term "quadratic termination" in this connection is inadequate.

<sup>\*\*</sup> The detailed mechanism of the reaction is as follows:

 $<sup>(3)</sup> C_2H_5 \longrightarrow C_2H_4 + H$ 

 $<sup>(9) 2</sup>C_2H_5 \longrightarrow C_4H_{10}$ 

is associated with the formation of two unstable intermediates—the free radicals  $R_1$  and  $R_2$ :

(1) 
$$M_1 \longrightarrow R_1 + M_2$$
  $k_1$   
(2)  $R_1 + M_1 \longrightarrow R_1 H + R_2$   $k_2$   
(3)  $R_2 \longrightarrow R_1 + M_3$   $k_3$   
(4)  $R_1 + R_2 \longrightarrow M_4$   $k_4$ 

By the principle of stationary states we obtain

$$\frac{d[R_1]}{dt} = k_1[M_1] - k_2[M_1][R_1] + k_3[R_2] - k_4[R_1][R_2] = 0$$
 (3.89)

and

$$\frac{d[R_2]}{dt} = k_2[M_1][R_1] - k_3[R_2] - k_4[R_1][R_2] = 0$$
 (3.90)

Combining the two equations, we find that

$$[R_2] = \frac{k_1 [M_1]}{2k_4 [R_1]}$$

Substituting the value of  $[R_2]$  obtained into Eq. (3.90), we obtain a quadratic equation for  $[R_1]$ :

$$2k_2 [R_1]^2 - k_1 [R_1] - \frac{k_1 k_3}{k_4} = 0$$

or

$$[R_1] = \frac{k_1 \pm \left(k_1^2 + 8\frac{k_1 k_2 k_3}{k_4}\right)^{1/2}}{4k_2} = \frac{k_1}{4k_2} + \left[\left(\frac{k_1}{4k_2}\right)^2 + \frac{k_1 k_3}{2k_2 k_4}\right]^{1/2}$$

Further, if the constant  $k_1$  is small, we obtain approximately, neglecting the terms that contain the ratio  $k_1/k_2$ :

$$[R_1] \approx \left(\frac{k_1 k_3}{2k_1 k_4}\right)^{1/2}$$

Now, according to the mechanism, we may write for the rate of disappearance of  $M_1$ :

$$-\frac{d[M_1]}{dt} = k_1[M_1] + k_2[R_1][M_1] = \left\{k_1 + k_2 \left(\frac{k_1 k_3}{2k_2 k_4}\right)^{1/2}\right\}[M_1]$$

which, as seen, is expressed by a first-order equation with the experimentally observed rate constant

$$k_{\rm I} = \left\{ k_{\rm I} + \left( \frac{k_1 k_2 k_3}{2k_4} \right)^{1/2} \right\}$$

In this connection, the reader should be warned once again that a distinction must be made between the molecularity, i.e., the number of molecules involved in the step leading to reaction, and the order of reaction. As seen from the examples given, many reactions that proceed by a complicated mechanism obey the

first-order law. They cannot however be called unimolecular; it would be pointless and highly erroneous.

In conclusion, it should be noted that although the stationary-state principle is rather fruitful in the field of investigations of the mechanisms of complex chemical transformations, it alone cannot yet provide an unambiguous answer to the question of the correctness of the suspected elementary steps. Further examples of its application may be found in Chapter 10 which is devoted to the kinetics of photochemical reactions.

## 3.7. The Application of the Basic Law of Kinetics to Reactions in Open Systems

Chemical reactions are most frequently conducted in reactors operating under the conditions of gas flow (the synthesis of ammonia, cracking processes, etc.). In these cases, the volume of the reaction mixture may undergo changes and therefore here use must be made of the general definition of the reaction rate (1.4):

$$w = \pm \frac{1}{V} \cdot \frac{dN}{dt}$$

We shall consider some of the specific features of mathematical equations for a reaction that takes place in the gas stream. Let us isolate mentally two planes 1 and 2 each of area 1 cm<sup>2</sup> in the stream, which are at a distance *dl* from each other and are perpendicular to the direction of the gas stream. We assume the temperature to remain constant along the entire length of the reaction zone. A possible diffusion transport of the substance is ignored.

Let the linear velocity of the gas current be equal to U cm/sec for the first plane (first in the direction of the gas current) and the concentration of one of the reactants,  $A_i$ , be equal to  $c_{A_i}$  moles/cm³. Then,  $c_{A_i}$  Udt moles of substance  $A_i$  will cross the first plane in time dt. A different amount of the same substance can cross the second plane even if no reaction takes place because, for example, of the accumulation of the substance in the volume under consideration, the expansion of the stream, etc. Suppose that the following amount of substance  $A_i$  will cross the second unit plane in the same time, dt:

$$\left[c_{\mathbf{A}_{l}}U - \frac{\partial\left(c_{\mathbf{A}_{i}}U\right)}{\partial l} dl\right]dt$$

Thus, the excess of the outcoming substance over the incoming quantity is

 $-\frac{\partial \left(c_{\mathbf{A}_{l}}U\right)}{\partial l}dldt$ 

If the following reaction takes place in the system under consideration

$$v_1 A_1 + v_2 A_2 + \dots = v_1' A_1' + v_2' A_2' + \dots$$

then the amount of gas  $A_i$  that entered the volume in question will differ from the amount of the gas that emerged because of the reaction having occurred too. Let the rate of the reaction in the given unit volume be W moles  $A_i/\text{cm}^3\cdot\text{sec}$ . Then, the total excess of the substance that emerged over the amount that entered will be

$$-\frac{\partial \left({}^{c}\mathbf{A}_{i}^{U}\right)}{\partial l} dl dt - w dl dt \tag{3.91}$$

and will be equal to the change of the total amount of the given substance in the given unit volume, i.e.,

$$\frac{\partial c_{\Lambda_i}}{\partial t} dl dt \tag{3.92}$$

Equating Eqs. (3.91) and (3.92), we obtain the relation

$$-\frac{\partial}{\partial l}\left(c_{\mathbf{A}_{i}}U\right) - w = \frac{\partial c_{\mathbf{A}_{i}}}{\partial t} \tag{3.93}$$

which is called the continuity equation and which expresses the law of conservation of matter. In a more general case of a non-linear problem the equation of continuity would have the form

$$-\operatorname{div}\left(c_{\mathbf{A}_{i}}U\right)-w=\frac{\partial c_{\mathbf{A}_{i}}}{\partial t}$$

We shall however be concerned here with a simpler problem, assuming that the reaction takes place in a tube or reactor under stationary or steady-state conditions, when the same quantity of the reaction mixture is supplied into the reaction zone in unit time. It is obvious that the substance will leave the reactor with a constant velocity as well. Under such stationary conditions in the reactor there will set in a distribution of the reacting substances that will be independent of time, i.e., for any substance in any volume element

$$\frac{\partial c_{\mathbf{A}_i}}{\partial t} = 0 \tag{3.94}$$

Under these steady-state conditions the concentration of any of the participants and the linear velocity of the gas in a given cross section of the reactor will be unambiguously determined by the initial values and the distance *l* from the given cross section to the entry into the reaction zone:

$$c_{\mathbf{A}_{l}} = f(l), \quad U = \varphi(l) \tag{3.95}$$

With account taken of Eq. (3.94), the continuity equation (3.93) is written as follows:

$$-\frac{d\left(c_{\mathbf{A}_{i}}U\right)}{dl} = w \tag{3.96}$$

Performing the differentiation of the product  $(c_{A_i} U)$ , we have

$$-U\frac{dc_{\Lambda_{i}}}{dl} - c_{\Lambda_{i}}\frac{dU}{dl} = \omega \tag{3.97}$$

All the quantities contained in this equation can be determined if the conditions of the process are specified. We now rearrange Eq. (3.97), introducing an expression for the concentration:

$$c_{\mathbf{A}_{i}} = \frac{N_{\mathbf{A}_{i}}}{V} \tag{3.98}$$

where  $N_{A_i}$  is the number of moles of substance  $A_i$ , passing through a given cross-sectional area in unit time, and V is the volume of the reaction mixture, which passes through the same reactor cross-section in the same time interval. We may also write an expression for the linear velocity of the gas:

$$U = \frac{V}{\rho} \tag{3.99}$$

if  $\rho$  is the cross-sectional area of the reaction tube.

Then we differentiate the concentration  $c_i$  (3.98) with respect to the distance l from the entry into the reaction zone:

$$\frac{dc_{A_i}}{dl} = \frac{1}{V} \cdot \frac{dN_{A_i}}{dl} - \frac{N_{A_i}}{V^2} \cdot \frac{dV}{dl}$$
(3.100)

The resulting derivative  $dc_{\Lambda_i}/dl$  is then substituted into expression (3.97). We get

$$-\frac{U}{V} \cdot \frac{dN_{A_i}}{dl} + \frac{U}{V} \cdot \frac{N_{A_i}}{V} \cdot \frac{dV}{dl} - c_{A_i} \frac{dU}{dl} = \omega$$
 (3.101)

Taking into account Eqs. (3.98) and (3.99) and assuming  $\rho$  to be constant along the entire length l, we become convinced that the second and third terms in (3.101) are equal and cancel out. We therefore obtain

$$-\frac{1}{\rho} \cdot \frac{dN_{A_l}}{dl} = \omega \tag{3.102}$$

If  $N_{0A_i}$  moles of substance  $A_i$  enters the reaction zone and  $x = (N_{0A_i} - N_{A_i})/N_{0A_i}$  represents a fraction of it that has reacted from the entry into the zone to point l (x = degree of conversion

or the extent of reaction), then, obviously,

$$N_{\mathbf{A}_{i}} = N_{0\mathbf{A}_{i}} (1 - x)$$

and

$$-\frac{dN_{A_i}}{dl} = N_{0A_i} \frac{dx}{dl}$$

Substituting this value of the derivative into Eq. (3.102) yields the following expression:

$$\frac{N_{0A_i}}{o} \cdot \frac{dx}{dt} = w$$

which is the basic equation of the kinetics of any chemical reaction in the stream. Here it is written in a general form and ought to be detailed with the aid of the basic law (1.8).

Thus, proceeding from expression (1.8), we may write for an irreversible reaction:

$$\frac{N_{0A_{i}}}{\varrho} \cdot \frac{dx}{dl} = kc_{1}^{p}c_{2}^{q}c_{3}^{r} \dots, \tag{3.103}$$

where  $c_1$ ,  $c_2$ , and  $c_3$  are the concentrations of the reactants  $A_1$ ,  $A_2$ , and  $A_3$ , ... And, accordingly, the following expression is derived for a reversible reaction:

$$\frac{N_{0A_i}}{\rho} \cdot \frac{dx}{dl} = k_1 c_1^p c_2^q c_3^r \dots - k_2 c_1'^{p'} c_2'^{q'} c_3'^{r'} \dots$$
(3.104)

Further in the text, for Eqs. (3.103) and (3.104) to be integrated, it is necessary to express the concentration  $c_{A_i}$  as a function of the distance l. The task is simplified if the reaction mixture may be regarded as an ideal-gas mixture. Then, the total volume of the mixture will be:

$$V = \sum_{i} N_{i} \frac{RT}{P} \tag{3.105}$$

and, hence, the concentration

$$c_{A_{i}} = \frac{N_{0A_{i}} (1 - x)}{\sum_{i} N_{A_{i}}} \cdot \frac{P}{RT}$$
 (3.106)

Here  $\sum N_{A_j}$  is the total number of moles of gaseous substances (both the reactants and products) that pass through the given cross-section of the reactor in unit time, and P is the pressure which depends, in a general case, on the distance l, i. e.,

$$P = \psi(l) \tag{3.107}$$

The total number of moles,  $\sum N_{A_j}$ , may be represented in the form of the following function of the degree of conversion x of substance  $A_i$ :

$$\sum N_{A_I} = N_{0A_I} (\alpha + \beta x) \tag{3.108}$$

where  $N_{0A_i}$  is the initial number of moles of the substance per unit time;  $\alpha$  is the inverse value of the mole fraction of substance  $A_i$  in the original system, i.e.,

$$\alpha = \frac{\sum N_{0A_f}}{N_{0A_f}} \tag{3.109}$$

and  $\beta$  is the change of the number of moles of gases in the reaction, which is calculated per one mole of substance  $A_i$ , i.e.,

$$\beta = \frac{v_i'}{v_i} + \frac{v_2'}{v_i} + \frac{v_3'}{v_i} + \dots - \frac{v_1}{v_i} - \frac{v_2}{v_i} - \frac{v_3}{v_i} \dots = \frac{\sum_{\text{final}} v_j' - \sum_{\text{initial}} v}{v_i}$$
(3.11)

When integrating kinetic equations (3.103) and (3.104) one must also know the mode of the change of pressure along the reactor, i.e., the function  $P = \psi(l)$ . Usually only the quantity  $\Delta P$  is specified, which is the difference between the pressures at the entrance and the exit of the reaction zone and it may be assumed that the pressure drop along the reactor is uniform,  $P = P_0(1-al)$ . It often suffices to assume the pressure in the reactor to be constant, putting  $\Delta P = 0$ . We shall confine ourselves to this last approximation.

And, finally, when integrating Eqs. (3.103) and (3.104) it is necessary to know the rate law expressing the dependence of the reaction rate on concentrations. We shall consider here only one of the simplest cases, namely, a first-order irreversible reaction since many cracking reactions of individual compounds belong to this category:

$$A = v_1'A_1' + v_2'A_2' + \dots$$

Equation (3.103) then assumes the form

$$N_{0A} \frac{dx}{\rho dl} = kc_A = k \frac{N_{0A} (1 - x) P}{\sum N_{Aj} RT}$$

In this particular case,  $\alpha$  from expression (3.109) is equal to unity and therefore

$$\sum N_{A_I} = N_{0A} (1 + \beta x)$$

Thus,

$$N_{0A} \frac{dx}{\rho dl} = k \frac{(1-x) P}{(1+\beta x) RT}$$

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$$N_{0A} \frac{RT}{P} \cdot \frac{dx (1 + \beta x)}{1 - x} = k\rho \, dl \tag{3.111}$$

In Eq. (3.111) the variables are separated and it remains only to integrate this equation from 0 to x and from 0 to l:

$$N_{0A} \frac{RT}{P} [-(1-\beta) \ln (1-x) - \beta x] = k\rho l = kV$$
 (3.112)

where  $V = \rho l$  is the volume of the reactor.

In kinetic studies, a series of experiments are usually conducted, in which the reactant  $A_{0A}$  is fed into the reactor at different rates, and the correspond-

ing degrees of conversion, x, are determined.

Equation (3.112) is rearranged, following which it has the form

$$N_{0A}x = -N_{0A} \frac{1+\beta}{\beta} \times$$

$$\times \ln(1-x) - k \frac{\rho V}{\beta RT}$$
 (3.113)

or

$$X = BY + C$$
 (3.114)

if the following notation is introduced:  $X = N_{0A}x$  and  $Y = -N_{0A} \ln(1-x)$ .

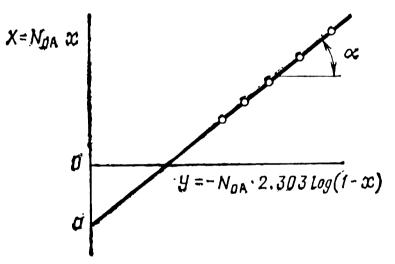


Fig. 3.7. The kinetics of a first-order reaction in the stream. A linear anamorphosis of formula (3.113).

Then, a graph is plotted, which shows the dependence of X on Y (Fig. 3.7). If a straight line is obtained, this is an indication that the assumption of first order is correct. The slope of the straight line,  $\tan \alpha = (1+\beta)/\beta$ , is used to find the coefficient  $\beta$ , owing to which it is not necessary to know the exact composition of the reaction products and to use Eq. (3.110). On the other hand, the  $\bar{O}a$  intercept is equal to  $-kpV/\beta RT$ . Hence, knowing  $\beta$ , the reactor volume V, the pressure and temperature, we can find the rate constant k.

We shall not consider other, more complicated cases here; the reader is referred to the original literature.

In conclusion, let us examine the simplest variant of a first-order reaction when it yields a single product, i.e.,

$$A \longrightarrow A'$$

In such a case,  $\alpha=1$  and  $\beta=0$  and Eq. (3.113) simplifies even more:

$$N_{0A} \frac{RT}{PV} \left[ -\ln\left(1 - x\right) \right] = k$$

Here  $N_{0A}RT/p = v$ , i.e., is equal to the volume of the gas that passes through the reactor per second. Evidently, v/V = 1/t, where t is the so-called time of contact. In this connection, we obtain the equation

$$\frac{1}{t} \ln \frac{1}{1-x} = k \tag{3.115}$$

which coincides in form with the simplest equation for a first-order reaction [Eq. (2.4)]. This is understandable since both equations have been obtained on the condition that the volume of the reacting system remains constant.

#### CHAPTER 4

# Effect of Temperature on Reaction Velocity

As known, the velocity of the vast majority of chemical reactions, with extremely rare exceptions such as the third-order oxidation of nitric oxide, increases rapidly with rise of temperature. It is exactly for this reason that heating is so widely used in chemical practice. It is important through what factors the temperature exerts an effect on reaction velocity. As a matter of fact, according to the basic law of kinetics, the reaction velocity is determined by the product

$$\mathbf{w} = k c_{\mathrm{A}}^{p} c_{\mathrm{B}}^{q} \dots$$

Thus, the temperature may, in principle, has an effect through a change in the concentrations, the exponents  $p, q, \ldots$ , and, finally, through a change in the rate constant k. Experiment shows that the possible change of reaction velocity caused by the first two factors is insignificant. The rate constant is affected most strongly by temperature; that is why, when speaking of the effect of temperature on reaction velocity, one usually implies the change of the rate constant.

The ratio of the rate constants found for a given reaction at temperatures t and  $t+10^{\circ}$ ,  $k_{t+10^{\circ}}/k_t$ , will be called here the temperature coefficient of the reaction rate. According to a simple empirical rule, the temperature coefficients of reaction velocities range from 2 to 4. In other words, an increase of  $10^{\circ}$  in temperature results in a 2- to 4-fold increase in the velocity of a chemical reaction. In the last formulation, which is, as a matter of fact, identical with the first, the regularity is known as the van't Hoff rule.

Since the temperature rarely changes by exactly 10°, it is useful to write the ratio of the constants at any two temperatures by expressing it in terms of the temperature coefficient:

$$\frac{k_{T+n10}}{k_T} = \gamma^n \tag{4.1}$$

where n may be positive, negative or fractional.

The van't Hoff rule provides a semi-quantitative characteristic of the effect of temperature; it is approximate and has been established for reactions in solutions, which proceed at relatively low temperatures. With rise of temperature  $\gamma$  does not remain constant: it diminishes and tends to unity.

The temperature dependence of the rate constant is more precisely expressed by the Arrhenius equation:

$$\ln k = -\frac{B}{T} + C \tag{4.2}$$

onstants characteristic of a particular reaction. Formula (4.2) which was originally derived by Svante Arrhenius in an empirical way is justified by a very large body of experimental data that refer to the diverse reactions both in gases and in solutions. It can also be obtained theoretically, as will be shown later, on the basis of certain thermodynamic premises and of the kinetic theory itself.

Let us now determine B and C from the values of the rate constants at two temperatures. Thus, for the decomposition of hydrogen iodide we have:

T. K
 
$$k$$
, cm³·mole $^{-1}$ ·sec $^{-1}$ 
 log  $k$ 

 556
 0.0003516
  $-3.454$ 

 781
 39.54
 1.597

On the basis of Eq. (4.2) we write the ratio of the rate constants:

$$\ln \frac{k_1}{k_2} = B \left( \frac{1}{T_1} - \frac{1}{r_1} \right)$$

or

$$B = \frac{2.303 \left(\log k_1 - \log k_2\right) T_1 T_2}{T_1 - T_2} = \frac{2.303 \left(1.597 + 3.454\right) 781 \times 656}{781 - 556} = 22,450$$

Now we shall determine the constant C at the two temperatures:

781 
$$C = 39.42$$
  
556°  $C = 32.43$ 

The values obtained are almost the same, which is an indication that C is really constant over a wide temperature range.

Thus, the temperature dependence of the rate constant for the decomposition of hydrogen iodide may be written in the final form (4.2):

$$\ln k = -\frac{22.450}{T} + 32.43 \text{ (cm}^3 \cdot \text{mole}^{-1} \cdot \text{sec}^{-1})$$
 (4.3)

Using relation (4.3), we can perform a simple, but interesting, calculation. The decomposition of hydrogen iodide proceeds with

a velocity convenient for measurements over a temperature range of 556-781 K. Let us determine the reaction rate constant at 100 °C (373 K):

$$\ln k = -\frac{22,450}{373} + 32.43$$

or

$$k = 8.83 \times 10^{-13} \text{ cm}^3/\text{mole} \cdot \text{sec} = 8.83 \times 10^{-16} \text{ litre/mole} \cdot \text{sec}$$

We now calculate the half-life of hydrogen iodide at this temperature, assuming the initial concentration to be equal to  $a = c_0 = 1$  mole/litre. Since this reaction is second order, we obtain from formula (2.19):

$$(T_{1/2})_{11} = \frac{1}{ak_{11}} = \frac{10^{16}}{8.83 \times 3600 \times 24 \times 365} = 3.6 \times 10^7 \text{ years}$$

Thus, without delving into the details of the thermodynamics of the process, we see that at 100 °C half of the volume of hydrogen iodide taken for the reaction would decompose in 36 million years. This is an astronomical period of time and there is absolutely no hope that at least traces of the decomposition will ever be detected. Such decreases of reaction velocity with decreasing temperature often lead to what is known as the kinetically frozen states. Thus, for example, a mixture of hydrogen and oxygen at room temperature is thermodynamically unstable and must be completely converted into water. To put it in a different way, in such a system there must occur processes leading to an equilibrium state. As might be expected, they do take place but proceed at such velocities which do not allow any changes in the system to be detected in a time period convenient for man. In the case of a kinetically frozen system, one sometimes speaks of a false equilibrium. This term is hardly suitable, the more so that, for example, when a suitable catalyst (spongy platinum in the case of oxyhydrogen gas) is used, the kinetic retardation is often eliminated and then the velocity of the reaction may be very great. The true state of equilibrium is not influenced at all by the catalyst.

Arrhenius substantiated his equation theoretically, proceeding from a thermodynamic relationship known as the van't Hoff isobar or isochore. The van't Hoff formula is known to express the temperature dependence of the equilibrium constant:

$$\frac{d \ln K_c}{dT} = \frac{Q}{RT^2} \tag{4.4}$$

Here we shall consider the original thermodynamic derivation of the Arrhenius equation since it allows one to understand well the effect of temperature on reaction velocity. The basic assumption made by Arrhenius consists in that not all the molecules can be involved in a reaction but only those which are in a special tautomeric form or active modification. Such activated molecules are formed from ordinary, normal molecules endothermically, i.e., with absorption of heat  $E_{\Lambda}$  (cal/mole). Consider, for example, the reaction

$$A \longrightarrow B$$

the velocity of which is expressed by the empirical equation

$$\frac{d[B]}{dt} = k[A] \tag{4.5}$$

where k is the observed rate constant which increases with temperature. According to Arrhenius, this reaction should be written in the form of two consecutive processes:

$$A + E_{\Lambda} \iff \Lambda_{act} \longrightarrow B \tag{4.6}$$

The second assumption made by Arrhenius is as follows. The formation of an activated molecule is invariably a reversible reaction; the concentration of the activated molecule corresponds to the thermodynamic equilibrium and it may, in principle, be defined through the equilibrium constant. Here it is evidently assumed that the conversion of the active modification (activated molecule) to the final product occurs relatively slowly and therefore the equilibrium concentration has time to be regained.

The third assumption is that the concentration of the active modification is always low and its formation practically has no bearing on the concentration of original molecules. In this connection, the equilibrium constant for the first reversible step of reaction (4.6) may be represented in a simplified form:

$$K_c = \frac{[A_{act}]}{[A]}$$
 or  $[A_{act}] = K_c[A]$  (4.7)

The isochore equation (4.4) may be applied to the equilibrium constant  $K_c$ :

$$\frac{d \ln K_c}{dT} = \frac{E_{\Lambda}}{RT^2} \tag{4.8}$$

The fourth and final assumption states that an activated molecule, once formed, is converted into the final product at a velocity which does not depend on temperature. Thus, according to Arrhenius, the role of temperature boils down to shifting the equilibrium between the normal and activated molecules, as a result of which the concentration of the latter increases. Taking into account the assumptions listed above, we may write the rate of

formation of the product:

$$\frac{d[B]}{dt} = \operatorname{const}[A_{act}] = \operatorname{const} K_c[A]$$

but, by virtue of Eq. (4.5), this velocity is equal to k[A].

Hence, according to Arrhenius, the rate constant k observed experimentally is expressed by the product of the equilibrium constant  $K_c$  and some other constant independent of temperature, i.e.,

$$k = \operatorname{const} K_c \tag{4.9}$$

Taking logarithms and differentiating Eq. (4.9) with respect to temperature, we obtain:

$$\frac{d \ln k}{dT} = \frac{d \ln K_c}{dT} \tag{4.10}$$

It is obvious that the derivative on the right-hand side may be replaced by the expression from Eq. (4.8). Thus, the following relation results:

$$\frac{d \ln k}{dT} = \frac{E_{\mathbf{A}}}{RT^2} \tag{4.11}$$

which is the Arrhenius equation in differential form.

The quantity  $E_{\Lambda}$  which has the dimensions of energy per mole and is the heat of formation \* of one mole of the activated molecule (active modification) in accordance with Eq. (4.6) was termed by Arrhenius the heat or **energy of activation.** For reasons that will be clear at a later time, we shall call  $E_{\Lambda}$  the experimental energy of activation.

Now we integrate Eq. (4.11), assuming  $E_A$  to be constant:

$$\ln k = -\frac{E_{\rm A}}{RT} + C \tag{4.12}$$

where C is the integration constant which is independent of temperature. Comparing Eq. (4.12) with the Arrhenius empirical equation (4.2), we become convinced that they are in full functional agreement. Further, evidently

$$B = \frac{E_{\Lambda}}{R} \quad \text{or} \quad E_{\Lambda} = BR \tag{4.13}$$

For the decomposition of hydrogen iodide B=22,450 and hence,  $E_{\rm A}=22,450\times 1.986=44,560$  cal/mole

Thus, for one mole of an activated molecule of hydrogen iodide to be formed from the normal molecules, it is necessary to consume 44,560 cal.

<sup>\*</sup> Here the thermodynamic convention is adopted—the heat absorbed is considered to be positive.

The Arrhenius equation is often represented in the following exponential form obtained from Eq. (4.12):

$$k = e^{-E_{A}/RT + C} = e^{C}e^{-E_{A}/RT} = 10^{0.4343C}e^{-E_{A}/RT}$$
(4.14)

Thus, the rate constant is expressed by the product of the preexponential factor (or the frequency factor) \*, which does not depend on temperature at a first approximation, and the exponential function which determines the temperature dependence. The following notation is usually introduced for the pre-exponential factor:

$$A = 10^{0.4343C}$$

Hence, the rate constant may be represented in the form

$$k = Ae^{-E_{\rm A}/RT} \tag{4.15}$$

So, for the reaction of decomposition of hydrogen iodide we obtain the formula

$$k = 1.2 \cdot 10^{14} \cdot e^{-44,560/RT} \text{ (cm}^3 \cdot \text{mole}^{-1} \cdot \text{sec}^{-1})$$

which satisfactorily describes the data given in Table 4.1. Analogous equations containing other constants are obtained for other reactions. Thus, for example, the dependence of the rate of the first-order reaction

$$N_2O_5 \longrightarrow N_2O_4 + \frac{1}{2}O_2$$

is expressed by the relation

$$k = 4.95 \times 10^{13} e^{-24.710/RT} (\text{sec}^{-1})$$
 (4.16)

Table 4.1 compares the experimental values of the constants with the values calculated from formula (4.16).

As can be seen from the data given in Table 4.1, Eq. (4.16) too defines satisfactorily the temperature dependence of the rate constant.

Now let us determine the experimental activation energy. The previously employed method of calculating  $E_A$  from two values of rate constants is not reliable. Use is more often made of the graphical method. In compliance with Eq. (4.2), the function  $\ln k = f(1/T)$  should give a straight line on the graph. It is the graph of  $\ln k$  (or  $\log k$ ) versus the inverse temperature which is plotted in practice (Fig. 4.1). The y intercept is equal to the constant C, and the constant B is determined from the slope:

$$\tan \alpha = -\tan \beta = -B$$

or

$$\tan \beta = B$$

<sup>\*</sup> It is sometimes referred to simply as the A-factor. — Tr.

FABLE 4.1. Comparison of the Rate Constants Calculated by the Arrhenius Equation (4.16) with Experimental Values for the Reaction  $N_2O_5 \longrightarrow N_2O_4 + \frac{1}{2}O_2$ 

	k <sub>1, s</sub>	sec-1		<i>k</i> <sub>I</sub> , s	ec-1
<i>T</i> , K	experimental data	calculated by formula (4.16)	Т, Қ	experimenta! data	calculated by formula (4,16)
273 288 293 298 308	$ \begin{array}{ c c c c c } \hline 7.87 \times 10^{-7} \\ 1.04 \times 10^{-5} \\ 1.76 \times 10^{-5} \\ 3.38 \times 10^{-5} \\ 1.35 \times 10^{-4} \end{array} $	$ \begin{array}{ c c c c c c } \hline 7.67 \times 10^{-7} \\ 0.82 \times 10^{-5} \\ 1.72 \times 10^{-5} \\ 3.43 \times 10^{-5} \\ 1.31 \times 10^{-4} \end{array} $	313 318 323 328 338	$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$

In some cases, the dependence of the rate constant on temperature is more complicated, as shown, for example, in Fig. 4.2. Such

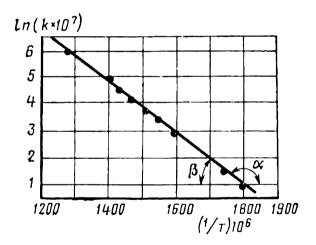


Fig. 41. The effect of temperature on the rate constant of the decomposition of hydrogen iodide.

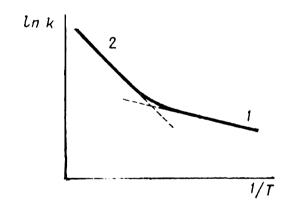


Fig. 4.2. The effect of temperature on the rate of a complex reaction:

1—the reaction with a lower  $E_{\mathbf{A}}$  predominates; —the reaction with a greater  $E_{\mathbf{A}}$  predominates.

a relationship indicates that the reaction is complex: it consists of two or more reactions which depend on temperature in different ways. The plot shown in Fig. 4.2 should be interpreted as one consisting of two intersecting straight lines with different slopes B. At low temperatures the reaction with a lower value of  $E_A$  predominates; at high temperatures it is the reaction with a larger value of  $E_A$  that prevails. Such a plot has been obtained, for example, in a study of the interaction of hydrogen and sulphur. In the experiments carried out by Norrish and Rideal, the reac-

tion vessel contained simultaneously liquid sulphur and its vapour. It was found that the reaction can take place with hydrogen interacting both with gaseous as well as liquid sulphur. In the former case,  $E_{\Lambda}$  is considerably greater. Therefore, curve 2 in Fig. 4.2 corresponds to a homogeneous reaction.

But what are the values of the activation energy for different reactions? The most usual values of  $E_{\rm A}$  for reactions between bond-saturated molecules are tens of thousands of calories per mole (Table 4.2).

TABLE 4.2. Experimental Energies of Activation for Selected Reactions of Bond-Saturated Molecules

Reaction	$E_{ extbf{A}}$ . kcal/mole
$2HI \longrightarrow H_2 + I_2$ $H_2 + I_2 \longrightarrow 2HI$ $2NO_2 \longrightarrow 2NO + O_2$ $2NOCI \longrightarrow 2NO + CI_2$ $N_2O_5 \longrightarrow N_2O_4 + \frac{1}{2}O_2$	44.56 39.6 27.0 26.5 24.7

It should be noted that the values given are based exclusively on experimental data since for reactions between bond-saturated

TABLE 4.3 The Energy of Activation of Selected Reactions Involving Free Atoms and Radicals

Reaction	E <sub>A</sub> , kcal/mo¹e	
$H + CH_1 \longrightarrow H_2 + CH_3$	13	
$H + C_2H_6 \longrightarrow H_2 + C_2H_5$	9.5	
$H + Cl_2 \longrightarrow HCl + Cl$	2	
$H + I_2 \longrightarrow HI + I$	0	
$H + HC1 \longrightarrow H_2 + C1$	4.5	
$H + HBr \longrightarrow H_2 + Br$	1.2	
$H + HI \longrightarrow H_2 + I$	1.5	
$OH + CH_4 \longrightarrow H_2O + CH_3$	8.5	
$OH + C_2H_6 \longrightarrow H_2O + C_2H_5$	5.5	
$CH_3 + CH_4 \longrightarrow CH_4 + CH_3$	11.2	
$CH_3 + C_2H_6 \longrightarrow CH_4 + C_2H_5$	10.4	
$Cl + H_2 \longrightarrow HCl + H$	5.6	
$Br + H_2 \longrightarrow HBr + H$	1.2	

molecules there have not been established simple regularities relating the energy of activation to some other characteristic of the reaction, say, to its heat.

Of great importance to kinetics is the decrease of the energy of activation upon passing over to reactions involving free atoms

and radicals (Table 4.3).

At identical temperatures the reaction with a lower energy of activation proceeds at a faster rate. Therefore, many reactions occur by elementary mechanisms with the participation of free atoms and radicals. Evans and Polanyi (1938) indicated the existence of a relation of the following type for such reactions:

$$E_{\Lambda} = A - \alpha Q$$

where A and  $\alpha$  are constants which are, generally speaking, different for different reactions, and Q is the heat of reaction. Considering that the accuracy of determination of  $E_A$  is not high enough for free radical reactions, N. N. Semenov, however, thinks it possible to suggest a general relationship between the energy of activation and the reaction heat:

$$E_{A} = 11.5 - 0.25 | Q | \text{ (kcal/mole)}$$

#### CHAPTER 5

# Elements of Statistical Thermodynamics

### 5.1. Entropy and Randomness of the State of a System

The second law of thermodynamics states the existence of a certain property of a system \*, S, associated with heat exchange and a temperature at which this heat exchange takes place:

$$dS \geqslant \frac{\delta Q}{T} \tag{5.1}$$

or, for an isolated system in the absence of heat exchange,

$$dS \geqslant 0$$
 (5.2)

The property S is known as the entropy. The meaning of relations (5.1) and (5.2), which were introduced by Clausius and which are a mathematical expression of the second law of thermodynamics, consists in that an increment in entropy may be either equal to the reduced heat (for equilibrium-reversible processes) or greater than the reduced heat (for non-equilibrium processes). Thus, entropy is as ociated, on the one hand, with heat exchange and, on the other, with irreversibility. In this lies the dual nature of entropy, which undoubtedly makes it difficult, at the very outset, to grasp the physical significance of this most important thermodynamic function. It appears, however, that it is this duality that helps one to eventually understand entropy but not from the standpoint of the Clausius classical propositions but from the viewpoint of molecular statistics developed at a later time.

Deferring for a while the quantitative treatment of the problem, we shall note that the dual nature of entropy can easily be understood if use is made of the concepts of the atomic-molecular structure of matter and if the state of the system is treated from the standpoint of the ordered-disordered motion or state of its constituent particles.

An example of, so to say, the ideal orderliness of molecular structure may be cited a well-developed crystal of a pure sub-

<sup>\*</sup> That is, a unique function of the state parameters of a system.

stance (say, of a metal) at a temperature close to absolute zero. As known, the atoms (or molecules) in such a crystal are arranged at some definite points in space, the crystal-lattice points, near which they perform *identical* vibrational motions with the so-called zero-point energy. According to Planck (the third law of thermodynamics) the entropy of such a crystal is equal to zero.

The ideal order is disturbed if the body is heated. On moderate heating an ever increasing number of particles appear, which vibrate with different energies, the mean position of particles in lattice points being still retained. The disturbance of the order (or the increase of disorder) associated with the heating of the body, leads to an increase in the entropy:

$$\Delta S = \int_{0}^{T} C \frac{dT}{T}$$

where C is the heat capacity.

The phase transitions solid  $\Rightarrow$  liquid and liquid  $\Rightarrow$  vapour, which are associated with the breakdown of the crystalline structure (melting) and with the formation, during the evaporation, of a system of weakly interacting and chaotically moving particles, are accompanied by an isothermal absorption of heat and a sharp increase in the entropy of the substance:

$$\Delta S_{\rm melt} = \frac{\Delta H_{\rm melt}}{T_{\rm melt}}$$
 and  $\Delta S_{\rm evap} = \frac{\Delta H_{\rm evap}}{T_{\rm evap}}$ 

The value of  $\Delta S$  is particularly high in the latter case, i.e., in the formation of the most disordered, chaotic state of aggregation, the vapour or gaseous state. Thus, there evidently exists a certain parallelism between the absorption of heat by the system, the increase in the disorder of its molecular structure, and the increase in the entropy. All the processes described above can be made to proceed reversibly, in which case we may utilize relation (5.1) with an equality sign.

But, according to Eq. (5.2), the increase in entropy of the system is also possible without any heat exchange in non-equilibrium processes. Suppose, for example, that in an isolated system there is a mechanism containing a compressed ("wound") spring and a device that releases it at a specified moment. When released the spring would be able to perform work, for example, would compress another spring and in this case, under the conditions of complete equilibrium, the entropy of the system will remain constant [the equality sign in relation (5.2)]. But the simply released spring uncoils without performing work. The potential elastic energy stored in the spring—the energy of the "ordered'

state—is transformed into the energy of the random motion of molecules, i.e., the system is heated. In such a non-equilibrium process the disorder of the molecular state of the system also increases and its entropy increases as well, but this time in the absence of absorption of heat from outside.

Let us consider, as a further example, an electric storage battery close-circuited automatically in an isolated system for resistance. In this case, the organized and directed energy of the electric battery, which could, in principle, be utilized for the performance of work, is transformed into Joule heat. The disorder of the molecular state of the system is increased. The entropy is thus increased as well.

By way of citing more examples, one can be convinced that in any non-equilibrium irreversible process there takes place the conversion of any organized form of energy (capable, generally speaking, of being converted quantitatively, by way of performing work, into another, also organized form) into the disordered energy of the random motion of molecules. In other words, in any such process the molecular chaos and, hence, the disorder of the molecular state of the system increases.

Thus, the entropy of the system increases in parallel with the increase of the chaos or "mixtupness" of its molecular state, irrespective of whether this disorder is associated with the absorption of heat or with the conversion of the organized energy into heat. Hence, the entropy may be regarded, from the qualitative standpoint, as a measure of the disorder ("mixtupness") of the molecular state of the system.

### 5.2. Macro- and Microstates of the System

The state of a system defined by a set of its thermodynamic properties, such as temperature, pressure, specific volume, etc., can now be conveniently called the **macrostate** in contrast to the **microstate**. The latter would be known if we, first, determined the spatial position of each molecule with the required degree of accuracy, i.e., its coordinates  $q_1, q_2, q_3 \dots q_f^*$  (altogether, f coordinates), and, second, established the mode of motion of each molecule at a given instant of time, i. e., if we indicated the momenta conjugated with the coordinates indicated,  $p_1, p_2, p_3 \dots p_f$  (altogether, f momenta).

Since the molecules are in motion and are colliding with one another, exchanging momenta, it is obvious that to a given mucrostate there will, generally speaking, correspond a large number

<sup>\*</sup> In the simplest case of a monatomic gas, three rectangular coordinates and, accordingly, three impulses will suffice.

of microstates. It is essential that the number of microstates be limited so that it is not infinitely large. For this to be done, it will suffice if we determine the coordinates and momenta of the particles not with absolute accuracy but only with the indication that these characteristics lie within the limits from  $q_i$  to  $q_i + dq_i$  and from  $p_i$  to  $p_i + dp_i$ .

It will be convenient to introduce the concept of a multi-dimensional space which has 2f dimensions, accordingly with f space coordinates and f momenta. A point in such a phase  $\mu$ -space will precisely define all the 2f characteristics of the molecule. To render a multitude of macrostates countable, the phase space is divided into elementary cells having the volume \*:

$$\omega = dq_1 \dots dq_f \cdot dp_1 \dots dp_f$$

and the state of the molecule is regarded as sufficiently definite if the corresponding representative point is in a given elementary cell.

In Boltzmann classical statistics, the macrostate of a system, for example, of any ideal gas, is characterized by indicating the number of representative points in the various cells of the phase space. For the microstate to be characterized in classical statistics, it is also necessary to specify the representative points of which molecules are in each cell. In other words, molecules are considered to be distinguishable and the interchange of two molecules which are in different cells will produce a new microstate without altering the macrostate.

Thus, the number of microstates corresponding to a given macrostate can be calculated if we find the number of different arrangements of representative points in cells.

Suppose a system consists of N molecules and to its macrostate there correspond  $N_1$  representative points in the first cell,  $N_2$  points in the second cell, and so on, and, in general,  $N_i$  points in the *i*th cell. Since the interchanges of positions within a cell are disregarded (they do not give rise to new microstates), the number of microstates is found as the number of exchanges with recurrences:

$$G = \frac{N!}{N_1! N_2! \dots N_i!}$$
 (5.3)

It will be useful to illustrate the method by a simple example. We shall only consider the distribution of molecules in an ordinary three-dimensional space. We shall confine ourselves to

<sup>\*</sup> In quantum statistics, using Heisenberg's uncertainty principle,  $dq \cdot dp \geqslant h$ , it is assumed that  $\omega = h^{l}$ . In classical statistics, the volume of an elementary cell remains undetermined.

six molecules and three cells

1	1, 2, 3 4, 5, 6		
11	1, 3	4, 6	5, 2

The above diagram shows two macrostates: I in which all the molecules are in one cell and II in which the molecules are uniformly distributed among all the cells. The number of microstates corresponding to the first macrostate is equal to unity: all the molecules are in the first cell, and the exchanges of positions within the cell are disregarded. For the second macrostate we calculate G from formula (5.3):

$$G = \frac{6!}{2! \ 2! \ 2!} = 90$$

that is, the second macrostate can be obtained in 90 ways, according to classical statistics. Even from the most general considerations it must be clear that the second state must be realized much more frequently. The number G calculated by the method described above from formula (5.3) is also called the number of arrangements.

#### 5.3. Thermodynamic Probability and Entropy

Statistical thermodynamics is based on the hypothesis of equal a priori probabilities: all the microstates of a system, which are compatible with the specified conditions (for example, with the condition of constancy of energy), are mathematically equally probable. At first glance, one may think that this hypothesis cannot correspond to reality. Indeed, let us compare two microstates of a mole of a gas. Suppose that in one state the gas mole occupies the entire volume of the vessel, say, 10 litres, and that its molecules are in chaotic motion. We shall assume that this microstate corresponds to an equilibrium macrostate. In the other microstate all the molecules accumulate in a volume of 1 cm<sup>3</sup> and are moving in parallel. Suppose that the spontaneous transition from the first equilibrium state to the second, non-equilibrium state is really difficult. But, nonetheless, the hypothesis of equal probabilities leads to correct consequences and is evidently valid. The point is how often each of the microstates is encountered.

to understand the essence of the problem it is useful to resort to a pack of 52 cards. Imagine also a machine that shuffles the whole pack once per second. As a result of this procedure, there may obtain any distribution of cards, including the ordered arrangements by seniority and by suits. The probability of any distribution (a "microstate") is equal. But the ordered distribution is the only one, and the number of disordered arrangements is

$$52! = 10^{30}$$
?

With the frequency of change of combinations being 1 sec<sup>-1</sup> each of these combinations, including the ordered one, will be encountered once in 10<sup>30</sup> years. Likewise, we could also compare the "recurrence" or the "waiting time" of the above-indicated microstates of the gas with the only difference that for a non-equilibrium state it is so enormously great that it is difficult to express it with the aid of ordinary methods of writing numbers; we may write, say, the number 10<sup>30</sup> raised to the power of 10<sup>30</sup>, but this will give little.

The conception of microstates and of their equal probabilities and also of the fact that to different macrostates there may correspond different numbers of microstates, leads to the idea of the thermodynamic probability for a state (a macrostate), W:

$$W = \text{const} \cdot G$$

to the number of microstates corresponding to a given macrostate. Moreover, we may assume the proportionality factor to be equal to unity and regard W as the relative probability, i.e., the probability of any particular state with respect to the probability of some standard state. The quantity W may also be regarded as the numerator of the mathematical probability, the denominator of which is the number of all the microstates conceivable for a given system, which are compatible with the laws of conservation. Thus,

$$W = G \geqslant 1 \tag{5.1}$$

the value of W being very great for ordinary molecular systems in a state of equilibrium.

The statistical meaning of the second law of thermodynamics consists, according to Boltzmann, in that an isolated system undergoes evolution predominantly in the direction of a greater thermodynamic probability. To put it in a different way, the second law of thermodynamics has no absolute value as the first law since the spontaneous formation of non-equilibrium states, say, the self-compression of a gas, is not absolutely impossible. The thermodynamic probability of such states is simply very low (they are represented by a small number of microstates) and the-

refore they are probably realized very rarely. As can be shown, the thermodynamic probability of a state of equilibrium for ordinary molecular systems, say, a gas mole, is found to be many times greater than the sum of thermodynamic probabilities of *all* possible non-equilibrium states:

$$W_{\text{(eq. state)}} \gg \sum_{\text{all}} W_{\text{(non-eq. state)}}$$

Thus, the system undergoes evolution to the side of an increase in the thermodynamic probability, and the equilibrium state corresponds to the greatest, maximum value of W. But it is exactly in this manner that the entropy of an isolated system is changed. Therefore, these quantities must be interrelated, i.e.,

$$S = f(W)$$

To establish the form of this function, let us consider two independent systems with the probabilities of states  $W_1$  and  $W_2$ . If a new composite system is built up of these two systems, its thermodynamic probability will be expressed, according to the theorem of multiplication of probabilities, by the product

$$W = W_1 W_2 \tag{5.5}$$

The entropies of the systems taken separately are functions of the probabilities:

$$S_1 = \int (W_1)$$
 and  $S_2 = \int (W_2)$ 

and the entropy of the composite system is equal to the sum of these entropies since S is an extensive, additive property of the system. So,

or 
$$S = S_1 + S_2 f(W) = f(W_1) + f(W_2)$$
 (5.6)

Likewise, according to Eq. (5.5),

$$f(W_1W_2) = f(W_1) + f(W_2)$$

The last expression is then differentiated first with respect to  $W_{12}$ 

$$W_2 f'(W_1 W_2) = f'(W_1)$$

and then with respect to  $W_2$ :

$$f'(W_1W_2) + W_1W_2f''(W_1W_2) = 0$$

or

$$f'(W) + Wf''(W) = 0$$

The last equation is rewritten in the following form:

$$1 + W \frac{f''(W)}{f'(W)} = 0 \qquad \text{or} \qquad \frac{f''(W)}{f'(W)} dW = -\frac{dW}{W}$$

Integrating, we find

$$\ln f'(W) = -\ln W + \ln k = \ln \frac{k}{W}$$

in which expression  $\ln k$  is the integration constant. Since with the logarithms being equal the logarithmic expressions are also equal, we may write down:

$$f'(W) = \frac{k}{W}$$

or, multiplying by dW,

$$\int'(W) dW = k \frac{dW}{W}$$

Integrating once again, we obtain:

$$f(W) = k \ln W + \text{const}$$

Or

$$S = k \ln W + \text{const}$$

But, by virtue of Eq. (5.6), the integration constant is here equal to zero. Therefore we can finally write the equation

$$S = k \ln W \tag{5.7}$$

which establishes the relation between the entropy and the thermodynamic probability, i.e., the equation known as the **Boltzmann equation**. It is the fundamental equation in statistical thermodynamics. In Eq. (5.7) the constant k is, strictly speaking, arbitrary, but we are interested in selecting a value

of this constant such that the entropy determined by this equation coincides with the ordinary, so to say, "thermodynamic" entropy of the second law.

Let us examine the process of isothermal expansion of an ideal gas from volume  $V_1$  to  $V_2$ . According to Eq. (5.7), the change of S will be given by the equality

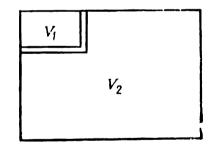


Fig. 5.1. Concerning the determination of Boltzmann's constant.

$$\Delta S = k \ln \frac{W_2}{W_1} \tag{5.8}$$

If the volumes  $V_1$  and  $V_2$  are represented as shown in Fig. 5.1, it will be clear that the probabilities of a single molecule residing in the final volume  $V_2$  or the initial volume  $V_1$  are interrelated as the volumes themselves, i.e.,  $V_2/V_1$ . If there are two molecules, the ratio of the probabilities will be equal to  $(V_2/V_1)^2$  and so on. Obviously, for a mole of a gas

$$\frac{W_2}{W_1} = \left(\frac{V_2}{V_1}\right)^{N_A}$$

where  $N_A$  is Avogadro's number equal to  $6.02252 \times 10^{23}$ . Thus, according to Eq. (5.8), the change of the entropy

$$\Delta S = kN_{\rm A} \ln \frac{V_2}{V_1}$$

But, on the other hand, the change of the entropy of one mole of an ideal gas upon isothermic expansion from  $V_1$  to  $V_2$  is defined by the well-known formula:

$$\Delta S = R \ln \frac{V_2}{V_1}$$

Therefore, for the statistical entropy to coincide with the thermodynamic entropy, it is necessary to put

$$k = \frac{R}{N_{\Lambda}} = 1.38045 \text{ erg/degree}$$

The quantity determined in this way is known as the **Boltzmann** constant. It is one of the universal physical constants.

Let us now return to the question of the qualitative treatment of the entropy of a system as a measure of the disorder of its state (Sec. 5.1). From the standpoint of the conceptions expounded in the present section, a quantitative measure of disorder is the thermodynamic probability or the number of microstates. From this point of view, the changes that take place in the system because, of the absorption of heat — through heating, melting, evaporation, etc. — may also be regarded as being associated with the increase of W, i.e., with the increase of the number of microstates corresponding to a new macrostate, say, a liquid as compared with a crystal. Hence, the Boltzmann formula can also be employed for the calculation of the change in the entropy of the system in processes involving heat exchange.

# 5.4. The Law of Distribution of Molecules Among Their Energy Levels (the Boltzmann Distribution Law)

In many sections of physics and physical chemistry, use is made of the law describing the distribution of molecules among their energy levels in an equilibrium molecular system. The use of this law is often helpful, even when, strictly speaking, the system is a non-equilibrium one but does not differ strongly from an equilibrium system. For instance, the theory of chemical kinetics makes use, in a number of cases, of the concept of the formation of a certain intermediate (or a transition state), which is relatively slowly converted into the final products. Therefore, the concentration of such an intermediate does not substantially differ from the equilibrium concentration and can be calculated, at a

first approximation at least, by the methods of thermodynamics. In general, it is in this way that the relation between kinetics and thermodynamics is obtained.

In this connection, the methods of statistical thermodynamics, which enable calculating the thermodynamic functions of a substance—a system consisting of a large number of molecules—on the basis of the molecular characteristics obtained by spectroscopy, electron diffraction, and other methods, are important not only in the field of thermodynamics proper. They also play an important part in chemical kinetics and, primarily, in the statistical calculation of reaction velocity (the theory of absolute reaction rates).

These methods are based on the law of distribution of molecules among their energy levels known as the **Boltzmann distribution law**. We shall now take up the derivation of this law.

Let the gaseous system under study consist of a very large number, N, of molecules. It possesses a total (internal) energy  $U^*$  and occupies a constant volume V. Thus, from the thermodynamic standpoint, the system is isolated (U = constant, V = constant).

We shall assume that all the molecules are chemically identical but may have different energies. In the simplest case, this is the energy of translational motion,  $\binom{1}{2}mc^2$ , where c is the velocity of the molecule and m is its mass.

The distribution of molecules among their energy levels is given by indicating the number of molecules:

$$N_1$$
 having energy  $\varepsilon_1$ 
 $N_2$ 
 $\varepsilon_2$ 
 $N_3$ 
 $\varepsilon_3$ 
 $\delta_i$ 
 $\delta_i$ 

and so on. Distributing the molecules among groups characterized by definite values of energy, we thereby introduce the quantum-theory concepts of definite quantized values of energy (energy levels). In this treatment, however, the intervals between adjacent levels are not yet limited in any way and may be as small as desired before rigorous quantum concepts are introduced. Therefore, this method of treatment is suitable equally well for both classical and quantum interpretations.

The total energy of the system will be expressed by the sum

$$U = E = N_1 \varepsilon_1 + N_2 \varepsilon_2 + N_3 \varepsilon_3 + \dots = \sum_i N_i \varepsilon_i = \text{constant}$$
 (5.10)

<sup>\*</sup> This quantity is often denoted by E in statistics.

which is constant by the condition specified. The total number of molecules is also constant:

$$N = N_1 + N_2 + N_3 + \dots = \sum N_i = \text{constant}$$
 (5.11)

But the separate numbers  $N_i$  may, generally speaking, vary.

In order to obtain the form of the distribution law most suitable for our task, we are to take into account some additional characteristics of the energy levels of molecules, which follow from experimental (spectral) data and also from quantum theory. The point is that a state of a molecule with a definite energy may also be characterized by other features or properties, which manifest themselves, for example, under the influence of a magnetic (Zeeman effect) or an electric (Stark effect) field. In other words, the same (or almost the same) energy value for a molecule can be attained in different ways, i.e., using the terminology of quantum mechanics, to one and the same energy of a molecule there may correspond several (g<sub>i</sub>) eigenstates.

In connection with what has been said above, we shall speak

In connection with what has been said above, we shall speak of the possibility of existence in the molecule of several energy levels of equal (or nearly equal) energy. Such multiple levels are known as **degenerate** levels and the degree of degeneracy  $g_i$  is also termed the **statistical weight** of the level or its **a priori probability**. The last two terms are evidently associated with the fact that degeneracy increases the total number of levels of given energy and, accordingly, increases the probability of appearance of molecules of given energy

of molecules of given energy.

Confining ourselves to the classical version of statistics, we shall assume that the state (macrostate) of the system is unambiguously determined by the distribution of distinguishable molecules among their energy levels, i.e., by indicating the numbers  $N_1$ ,  $N_2$ ,  $N_3$  ... of molecules having the energies  $\varepsilon_1$ ,  $\varepsilon_2$ ,  $\varepsilon_3$  ...

To compute the thermodynamic probability of a state, i.e., the number of ways it is realized, we shall first write the number of ways of distributing N molecules among i groups, i.e., energy states. This number is given by relation (5.3), i.e.,

$$\frac{N!}{N_1! N_2! N_3! \dots N_f! \dots}$$

However, within each group characterized by a definite energy,  $N_i$  distinguishable molecules in classical statistics may be arranged, without restrictions, among  $g_i$  levels. It is obvious that one molecule can be disposed in  $g_i$  levels by  $g_i$  ways, two molecules by  $g_i^2$  ways, etc. Hence, for  $N_i$  molecules the number of ways for their distribution among the levels will be equal to  $g_i^{N_i}$ .

The total number of microstates, i.e., the thermodynamic probability of a given macrostate, is obtained by multiplying the number of distributions among groups, which has been found above, by the numbers of distributions within the groups. Namely,

$$W = G = N! \frac{g_1^{V_1}}{N_1!} \frac{g_2^{N_2}}{N_2!} \dots \frac{g_j^{N_j}}{N_j!} = N! \prod \frac{g_i^{V_i}}{N_i}$$
 (5.12)

To the equilibrium state of an isolated system there corresponds the maximum of entropy S from the thermodynamic standpoint and the maximum of the thermodynamic probability W from the statistical standpoint. The relation between S and W is given by the Boltzmann formula (5.7):

$$\frac{S}{k} = \ln W \tag{5.13}$$

Substituting the value of W from Eq. (5.12) into this expression, we obtain:

$$\frac{S}{k} = \ln N! + \sum_{i} (N_{i} \ln g_{i} - \ln N_{i}!)$$
 (5.14)

The numbers N and  $N_i$  are usually considered to be very large and therefore Stirling's formula, which is the more exact the greater is N, may be applied to the factorials:

$$N! = \left(2\pi N\right)^{1/2} \left(\frac{N}{e}\right)^{N}$$

or

$$\ln N! = \frac{1}{2} \ln (2\pi N) + N \ln N - N$$

The last relation may be simplified for large N without appreciable error by eliminating the first term on the right-hand side:

$$\ln N! = N \ln N - N \tag{5.15}$$

Now the expression for the entropy (5.14) may be written thus:

$$\frac{S}{k} = N \ln N - N + \sum_{i} (N_{i} \ln g_{i} - N_{i} \ln N_{i} + N_{i}) =$$

$$= N \ln N + \sum_{i} (N_{i} \ln g_{i} - N_{i} \ln N_{i})$$
(5.16)

As we have already said, to the equilibrium there correspond the maximum values of W and S. Within the framework of the problem under consideration, the condition of equilibrium will be such that with all the permissible changes of the numbers  $N_i$  the sum

of the corresponding changes of entropy is equal to zero:

$$\sum dS_i = \delta S = 0$$

that is, the entropy does not change, remaining maximal. We now seek to find the partial entropy changes:

$$dS_1 = \frac{\partial S}{\partial N_1} dN_1 = -k \left( \ln \frac{N_1}{g_1} + 1 \right) dN_1$$
  
$$dS_2 = \frac{\partial S}{\partial N_2} dN_2 = -k \left( \ln \frac{N_2}{g_2} + 1 \right) dN_2$$

and so on. Summing up all the partial entropy changes, we obtain its total change:

$$\delta S = \sum_{i} dS = -\sum_{i} k \left( \ln \frac{N_i}{g_i} + 1 \right) dN_i$$
 (5.17)

It is obvious that the condition of the equilibrium for the molecular system under consideration is the equality

$$\sum_{i} \left( \ln \frac{N_i}{g_i} + 1 \right) dN_i = 0 \tag{5.18}$$

The variables  $N_i$  are not all independent since the numbers of molecules are interrelated by conditions (5.10) and (5.11) which may be represented in the form:

$$\delta N = \sum dN_i = 0$$

$$\delta U = \sum \epsilon_i dN_i = 0$$
(5.19)

Using the last equations, one can easily express two of the quantities  $dN_i$  as functions of all the remaining ones. Therefore, all the changes of  $N_i$ , except for two changes, may be considered to be independent. In order to eliminate the dependent changes, we shall make use of the method of undetermined. Lagrange multipliers. We shall multiply Eqs. (5.19) for  $\delta N$  and  $\delta U$ , respectively, by  $\lambda$  and  $\mu$  and sum up with (5.18). We obtain

$$\sum_{i} \left( \ln \frac{N_i}{g_i} + 1 + \lambda + \mu \varepsilon_i \right) dN_i = 0$$
 (5.20)

The arbitrary multipliers  $\lambda$  and  $\mu$  can always be selected such that two of the coefficients at  $dN_i$  in expression (5.20) vanish. Put, for example,

$$\ln \frac{N_1}{g_1} + 1 + \lambda + \mu \varepsilon_1 = 0 \quad \text{and} \quad \ln \frac{N_2}{g_2} + 1 + \lambda + \mu \varepsilon_2 = 0$$

Then the sum (5.20) will retain only those terms which contain the independent variations of the numbers of molecules,  $dN_i$ , and

the general equality of (5.20) to zero can be satisfied only if each of the remaining i-2 coefficients is equal to zero.

Thus, in general, for an equilibrium isolated system consisting of N weakly interacting molecules the following equality is valid:

$$\ln \frac{N_i}{g_i} + 1 + \lambda + \mu \varepsilon_i = 0 \tag{5.21}$$

Raising to a power, we obtain

$$N_i = \frac{g_i}{e^{(1+\lambda)}e^{\mu\varepsilon_i}} = \frac{g_i}{Be^{\mu\varepsilon_i}}$$

or

$$N_{i} = \frac{1}{R} g_{i} e^{-\mu \epsilon_{i}}$$

Here, evidently, the notation  $B = e^{1+\lambda}$  is introduced.

Expression (5.22) is the law of distribution of molecules among their energy levels (written in a general form) in Maxwell-Boltzmann classical statistics.\*

Further, we are to find the values of the coefficients B and  $\rho$ . To do this, we first add up all the numbers of molecules determined by relation (5.22). We get

 $N = \sum_{i} N_{i} = \frac{1}{B} \sum_{i} g_{i} e^{-\mu e_{i}}$   $\frac{1}{B} = \frac{N}{\sum_{i} g_{i} e^{-\mu e_{i}/kT}}$ 

Hence,

and the distribution law assumes the form

$$N_i = N \frac{g_i e^{-\alpha \varepsilon_i}}{\sum_i g_i e^{-\alpha \varepsilon_{ii}/\epsilon T}}$$
 (5.23)

It now remains to find the value of  $\mu$  that would satisfy the properties of a molecular system. To do this, we take logarithms in

<sup>\*</sup> In quantum statistics, which assume the indistinguishability of particles, the distribution law takes a somewhat different form. Namely,  $N_i = g_i/(Be^{\mu\epsilon_i}-1)$  in Bose-Einstein statistics, and  $N_i = g_i/(Be^{\mu\epsilon_i}+1)$  in Fermi-Dirac statistics. If B is sufficiently large, which is the case at all temperatures for ordinary molecular systems (except for helium), the unity in the denominator may be neglected, in which case both Bose-Einstein statistics and Fermi-Dirac statistics give the distribution law coinciding with the classical law. Comparing the formula given with (5.22) it is sometimes said that quantum statistics "differs" from classical statistics "by unity".

expression (5.23):

$$\ln N_i = \ln N + \ln g_i - \mu \varepsilon_i - \ln \left( \sum g_i e^{-\mu \varepsilon_i / kT} \right)$$
 (5.24)

Then, we multiply Eq. (5.24) by the number of molecules  $N_i$  and sum up all the expressions of this kind:

$$\sum N_i \ln N_i = \sum N_i \ln N + \sum N_i \ln g_i - \sum \mu N_i \epsilon_i - \sum N_i \ln \left(\sum g_i e^{-\mu \epsilon_i}\right)$$

With relations (5.10), (5.11), and (5.16) taken into account, the last equation may be represented in the following form:

$$N \ln N + \sum_{i} (N_i \ln g_i - N_i \ln N_i) = \mu U + N \ln \left( \sum_{i} g_i e^{-i\epsilon_i} \right) = \frac{S}{k}$$
 (5.25)

or

$$\frac{S}{k} = \mu U + N \ln \left( \sum g_i e^{-\mu \varepsilon_i} \right) \tag{5.26}$$

where U is the total energy and S is the entropy of the system of N molecules under consideration. If we now differentiate Eq. (5.26) with respect to the entropy at constant volume, then, considering the last term to be independent of S, we obtain

$$\frac{1}{k} = \mu \left( \frac{\partial U}{\partial S} \right)_{V} \tag{5.27}$$

But U, the total (internal) energy of the system, is a characteristic function of the variable entropy and volume, i.e., S and V, its exact differential dU = T dS - p dV, and therefore, as is known,

$$\left(\frac{\partial U}{\partial S}\right)_V = T \tag{5.28}$$

Hence, comparing Eqs. (5.27) and (5.28), we have

$$\mu = \frac{1}{kT} \tag{5.29}$$

where k is Boltzmann's constant defined carlier. Thus, Eq. (5.29) may now be represented in the form:

$$N_i = \frac{1}{B} g_i e^{-\epsilon_i/kT} \tag{5.30}$$

This formula is usually called the **Boltzmann** distribution law, which may be read as follows: for a molecular system at equilibrium, the number of molecules of energy  $\varepsilon_i$  is proportional to the **Boltzmann** factor  $e^{-\varepsilon_i/kT}$ .

The exponential Boltzmann law is one of the important generalizations in physics and finds numerous applications in its various branches. It is of fundamental importance in statistical thermodynamics and also in the theories of chemical kinetics.

The pre-exponential factor in the Boltzmann equation, 1/B, depends, as will be shown in the subsequent treatment, on temperature and also on the number and nature of molecules of which the system is composed. If the inference is repeated for a system containing, say,  $N_1$  molecules of substance I and  $N_{11}$  molecules of substance II, two exponential expressions obtain:

$$N_i = \frac{1}{B_I} g_i e^{-\varepsilon_i/kT} \tag{5.31}$$

and

$$N_{j} = \frac{1}{B_{II}} g_{j} e^{-\varepsilon_{j}/kT} \tag{5.32}$$

from the consideration of which it follows that if the value of 1/B is determined by the properties of the substance, then k is the universal constant.

#### 5.5. Evaluation of the Molecular Partition Function

Eliminating the factor 1/B from Eq. (5.30), as we have already done, we write the Boltzmann law in the form:

$$N_{i} = N \frac{g_{i}e^{-\varepsilon_{i}/kT}}{\sum_{i} g_{i}e^{-\varepsilon_{i}/kT}}$$
(5.33)

or

$$N_i = N \frac{g_i e^{-\varepsilon_i/kT}}{Q}$$

The most important quantity  $Q = \sum g_i e^{-\epsilon_i/kT}$  is called the partition function and is the sum of Boltzmann factors written for all the possible energy states of a molecule. In an extended form the partition function for an individual molecule (the molecular partition function) is written thus:

$$Q = g_1 e^{-\epsilon_1/kT} + g_2 e^{-\epsilon_2/kT} + g_3 e^{-\epsilon_3/kT} + \dots$$
 (5.34)

The partition function may be written somewhat differently if the lowest-energy state of a molecule is called the zero state and the corresponding energy, the zero energy  $\varepsilon_0$ , and the degeneracy of the zero level is designated as  $g_0$ :

$$Q = g_0 e^{-\epsilon_0/kT} + g_1 e^{-\epsilon_1/kT} + g_2 e^{-\epsilon_2/kT} + \dots = \sum_{i} g_i e^{-\epsilon_i/kT}$$
 (5.35)

where, as has already been said, the summation is carried out over all the possible energy states of the molecule.

In the partition function (5.35) the Boltzmann factors diminish rapidly with increasing  $\varepsilon_i$  (the exponential function!) and the

series expressing Q converge rapidly. Therefore, though, in principle, the summation must be carried out to infinity, in practice one may confine himself to a small number of terms and, in some cases, even to a single term.

The Boltzmann law (5.33) may now be written in the form

$$\frac{Q}{N} = \frac{g_i e^{-\varepsilon_i/kT}}{N_i}$$

In accordance with this relation, the partition function is related to the total number of molecules in the same way as the Boltzmann factor taken  $g_i$  times is related to  $N_i$ , which is the number of molecules of energy  $\varepsilon_i$ . Thus, the partition function may be looked upon as the generalized Boltzmann factor characterizing the total number of molecules of a given species in the system.

From the foregoing it is clear that the partition function has no dimensions, it helps one to describe, in a convenient mathematical form, the distribution of energy among the molecules in the system. The numerical value of Q, as will be seen later, depends on the molecular weight, temperature, the volume of the system, i.e., the volume in which the molecule is moving, the internuclear distances, and the mode of molecular motion.

## 5.6. The Partition Function of a System in Classical and Quantum Statistics

As will be shown later (Sec. 5.7), the partition function may be tied up with the thermodynamic properties of a system. However, if the thermodynamic functions of an ideal gas were determined from the molecular partition function, no accurate results would be obtained. Indeed, if correct values were obtained for the internal (total) energy, heat capacity and pressure, then the calculated entropy, for example, would be lower than the experimental value by about two entropy units (ca. 2 cal/degree·mole). Careful examination of the question shows that there is no sufficient ground for attempting to calculate the entropy and a number of other thermodynamic functions including entropy, which are, as a matter of fact, the properties of the system as a whole, on the basis of the molecular partition function Q. The necessary detailing leads to the understanding of the partition function of the system.

When considering the state of a system as a whole as a function of the states of its constituent particles (molecules), two cases must be distinguished. In the first case, the properties of the system are believed to depend on which individual particles exhibit which characteristics, i.e., in this case, the particles are

considered to be distinguishable. In the second case, the properties of the system depend only on the number of particles distributed among groups according to the characteristics displayed by them. The particles themselves are indistinguishable.

Let us consider the first case.

(a) Distinguishable particles. The Maxwell-Boltzmann system. Let the system consist of N identical molecules; each molecule may have an identical series of energy states. We consider the particles to be distinguishable, so that the state of the system as a whole must be characterized by indicating the state of each of N identical, distinguishable particles. According to the terminology adopted, this kind of system is called the Maxwell-Boltzmann system.

If we designate the states of N individual particles by  $i_1, i_2, \ldots, i_N$ , then in the absence of any interaction between them the energy of the system will be expressed by the relation:

$$E_{i_1, i_2, i_S, \dots i_N} = \varepsilon_{i_1} + \varepsilon_{i_2} + \varepsilon_{i_S} + \dots + \varepsilon_{i_N}$$

Each of the different specifications of values for the subscripts  $i_1, i_2, \ldots, i_N$  would correspond to an individual state of the system as a whole.

The partition function of the system is written in the following form:

$$\mathcal{F} = \sum_{i_1, i_2 \dots i_N} e^{-\left(\epsilon_{i_1} + \epsilon_{i_2} + \dots + \epsilon_{i_N}\right)/kT}$$
(5.36)

where the summation is carried out over all the possible values of  $i_1, i_2, \ldots, i_N$ .

The expression for  $\mathscr{F}$  may be immediately simplified by factorizing into the product of factors of the type  $e^{-\epsilon_i/kT}$  since the set of energy states is the same for all the molecules. Thus,

$$\mathscr{F} = \left(\sum_{i} e^{-\varepsilon_{i}/kT}\right)^{N} = Q^{N} \tag{5.37}$$

Here  $\varepsilon_i$  is the energy state of a single molecule and therefore Q is the molecular partition function. In writing relation (5.37) we imply the summation over i separate levels. With the degeneracy taken into account, when several levels are of the same energy, the formula obtained may be rewritten in the form

$$\mathcal{F} = \left(\sum_{i} g_{i} e^{-\epsilon_{i}/kT}\right)^{N} \tag{5.38}$$

where  $g_i$ , as before, denotes the number of distinguishable levels of the same energy  $\varepsilon_i$ .

We have thus obtained an expression for the partition function of a Maxwell-Boltzmann system consisting of N distinguishable non-interacting particles.

(b) Indistinguishable particles. Bose-Einstein and Fermi-Dirac gases. Dealing once more with a system (a gas) consisting of Nidentical particles, we shall assume that the state of the system as a whole is determined by simply indicating the number of particles in their various possible states. In contrast to Maxwell-Boltzmann statistics, here it is immaterial which particles are in which state. In other words, the particles are considered to be indistinguishable. It should be pointed out at this stage that this method of treatment indicates the possibility of existence of special, so-called degenerate states of the system. Here the term "degenerate" is used in quite a different sense than in the preceding section and refers to the system as a whole. This type of degeneracy manifests itself at low temperatures and high pressures and it does so the more readily the smaller the mass of the particles: for one thing, the outcome of it is that even upon approach to absolute zero the entropy and heat capacity become equal to zero. It is not our task to consider this type of degeneracy here since we may confine ourselves to sufficiently rarified gases which are at not too low a temperature.

Generally, in statistics the terms degeneracy and degenerate are used in three different senses and this should be kept in mind. First, the degeneracy is the number of energy levels having the same energy, i.e., the multiplicity of energy equations or their statistical weight, or multiplicity (as referred to electronic states).

Second, there is the quantum degeneracy of the system, when classical statistics becomes invalid and recourse has to be made to quantum statistics. This kind of degeneracy practically reveals itself at low temperatures in the helium isotope <sup>4</sup>He, and in the case of other gases it is masked by an intermolecular interaction, this kind of interaction being weak in helium.

And, finally, one speaks of the degeneracy of a motion. For instance, at moderate temperatures no vibrational motion of diatomic molecules occurs, i. e., it is degenerate. A consequence of this is their heat capacity  $C_v = (5/2)R$ .

So, let us consider a sufficiently rarefied gas consisting of N non-interacting particles, each of which may be in states having the energies  $\varepsilon_k$ ,  $\varepsilon_l$ ,  $\varepsilon_m$ ..., these states being common to all the particles.

Using the symbols  $\varepsilon_1, \varepsilon_2, \ldots, \varepsilon_N$  to designate the possible values of the energies of N molecules making up the system, we write the energy of the system in the form of the sum:

$$E = \varepsilon_1 + \varepsilon_2 + \ldots + \varepsilon_N \tag{5.39}$$

The total number of terms in the sum on the right-hand side is evidently N. Denoting then the numbers of molecules in the same energy states, by  $N_k$ ,  $N_l$ ,  $N_m$  ... [they designate the numbers of recurring terms and sums (5.39)], we find that the reduced value of E can be obtained by

$$\frac{N!}{N_k! N_l! N_m!}$$

ways by simply exchanging the subscripts  $1 \dots N$  for the energies  $\varepsilon_i$ . In the preceding section, when dealing with a system consisting of distinguishable particles, we thought that such transpositions would lead to different states of the system as a whole. In this case, however, since the particles are considered to be indistinguishable, this expression implies only the number of *identical states*. On the basis of what has been said, we may write the partition function for a system (an ideal gas) consisting of N identical indistinguishable elements:

$$\mathcal{F} = \sum_{\epsilon_1, \ \epsilon_2, \dots, \ \epsilon_N} \frac{N_k! \ N_l! \ N_m!}{N!} e^{-\frac{\epsilon_1 + \epsilon_2 + \dots + \epsilon_N}{kT}}$$
(5.40)

where the pre-exponential factor excludes the possibility of taking into account identical states in the partition function more than once.

Further, considering the application of expression (5.40), two cases may be distinguished. In the first case, the summation is carried out over all the possible values  $\varepsilon_1, \ldots, \varepsilon_N$ . This method is used in Bose-Einstein statistics originally developed by Bose for light quanta and applied by Einstein to gas molecules. In the second case, use is made of Pauli's exclusion principle, according to which the terms in which two or more values of energies  $\varepsilon_1$ ,  $\varepsilon_2, \ldots, \varepsilon_N$  refer to the same state. In such cases we speak of Fermi-Dirac statistics worked out for an electron gas.

Let us now consider the simplified expression (5.40), applying it to a gas which is at a sufficiently high temperature and occupies a large volume. Since there are a very large number of energy states, it may be assumed that there is not more than one molecule per each state. This allows us to set all the factorials  $N_k!$ ,  $N_l!$ ,  $N_m!$ ... equal to unity. Thus, for any kind of gas we obtain the following partition function as a satisfactory approximation:

$$\mathcal{F} = \frac{1}{N!} \sum_{e_1, e_2, \dots, e_N} e^{-\frac{e_1 + e_2 + \dots + e_N}{kT}}$$
(5.41)

in which all the possible values of  $\varepsilon$  for the energies of N particles are taken into account. However, the expression being summed can be factorized into the product of factors of the type  $\exp(-\varepsilon_k/kT)$  and rewritten thus:

$$\mathcal{F} = \frac{1}{N!} \left( \sum_{k} e^{-\epsilon_k/kT} \right)^N \tag{5.42}$$

In this new expression the summation is carried out over all the energy states of the only molecule of the type under discussion. If it is desirable, one can also take into account the multiplicity (degeneracy) of energy levels and write the partition function of an ideal gas consisting of N identical molecules in the following form:

$$\mathcal{F} = \frac{1}{N!} \left( \sum_{i} g_{i} e^{-\frac{\varepsilon_{i}}{kT}} \right)^{N} = \frac{1}{N!} \left( Q \right)^{N}$$
 (5.43)

Now the summation is carried out over all the energy levels and not over each individual state. Comparing expression (5.43) with the one derived earlier, (5.38), we see that the condition of the indistinguishability of particles leads to the appearance of an additional factor, 1/N!, in the partition function of the system.

If we take logarithms of  $\mathcal{F}$  from Eq. (5.43), we get

$$\ln \mathcal{F} = N \ln Q - \ln N^{\epsilon}$$

or, using Stirling's formula  $\ln N! = N \ln N - N + \frac{1}{2} \ln 2\pi N$ ,

$$\ln \mathcal{F} = N \ln Q - N \ln N + N - \frac{1}{2} \ln 2\pi N = N \left( \ln Q - \ln N + 1 - \frac{1}{2N} \ln 2\pi N \right)$$

The last term in parenthesis tends to zero with increasing N and we ignore it, assuming N to be very large.

We obtain

$$\ln \mathcal{F} = N \ln \frac{Qe}{N} \tag{5.44}$$

For the sake of brevity we shall call the partition function of the system  $\mathcal F$  the grand partition function.

## 5.7. The Partition Functions, Thermodynamic Functions and the Equilibrium Constant

Total (Internal) Energy and Enthalpy. To calculate the total energy of a system, we differentiate the grand partition function (5.43) with respect to temperature at constant volume. We obtain

$$\left(\frac{\partial \mathcal{F}}{\partial T}\right)_{V} = \frac{N}{N!} Q^{N-1} \left(\frac{\partial Q}{\partial T}\right)_{V} = \frac{N}{N!} Q^{N-1} \left(\frac{g_{1} \varepsilon_{1}}{k T^{2}} e^{-\frac{\varepsilon_{1}}{k T}} + \frac{g_{2} \varepsilon_{2}}{k T^{2}} e^{-\frac{\varepsilon_{2}}{k T}} + \dots\right)$$

We multiply the derivative by  $kT^2$  and divide by  $\mathcal{F}$ :

$$kT^{2} \frac{\partial \ln \mathcal{F}}{\partial T} = kT^{2}N \frac{\partial \ln Q}{\partial T} =$$

$$= \left(\frac{g_{1}\varepsilon_{1}}{Q} e^{-\frac{\varepsilon_{1}}{kT}} + \frac{g_{2}\varepsilon_{2}}{Q} e^{-\frac{\varepsilon_{2}}{kT}} + \dots + \frac{g_{i}\varepsilon_{i}}{Q} e^{-\frac{\varepsilon_{i}}{kT}}\right)N$$

Since further, according to Eq. (5.36),  $g_i e^{-\epsilon_i/kT} Q = N_i/N$ , we have for 1 mole of gas  $(N = N_A \text{ and } kN_A = R)$ :

$$kT^{2} \frac{\partial \ln \mathcal{F}}{\partial T} = RT^{2} \frac{\partial \ln Q}{\partial T} = (\varepsilon_{1}N_{1} + \varepsilon_{2}N_{2} + \ldots + \varepsilon_{i}N_{i}) = \sum_{i} \varepsilon_{i}N_{i} = U$$

Thus, the total (internal) energy is equal to

$$U = E = kT^{2} \left( \frac{\partial \ln \mathcal{F}}{\partial T} \right)_{V} = RT^{2} \left( \frac{\partial \ln Q}{\partial T} \right)_{V}$$
 (5.45)

It should be kept in mind that we calculate not the absolute value of total energy, as it might seem to be the case, but the excess of energy over a certain zero level  $U_0$  (or  $E_0$ ) which is most conveniently assumed to be the energy at absolute zero. Properly speaking, the values of the energy of a molecule, as represented by the series (5.9), should be written in the following form:  $\varepsilon_1 + \varepsilon_0$ ,  $\varepsilon_2 + \varepsilon_0$ ,  $\varepsilon_3 + \varepsilon_0$ , ..., where  $\varepsilon_0$  is essentially the indeterminable value of the zero energy of the molecule. With this comment taken into account, the expression for the total (internal) energy of the system should be written thus:

$$U - U_0 = E - E_0 = kT^2 \left( \frac{\partial \ln \mathcal{F}}{\partial T} \right)_V = RT^2 \left( \frac{\partial \ln Q}{\partial T} \right)_V$$
 (5.46)

In connection with these formulas it may be noted that the use of the grand and molecular partition functions gives in this case similar formulas which differ only in the factors k and R (when calculated per 1 mole). Later on, in calculating the individual partition functions (Sec. 5.10), it will be shown that the quantity RT/P is included as a cofactor in Q. Therefore we may writer

$$Q = q' \frac{RT}{P} = q'V$$
 and  $\ln Q = \ln q' + \ln \frac{RT}{P}$ 

As can easily be seen, the derivatives of  $\ln Q$  with respect to temperature at V= constant and P= constant have different values. Thus, if

$$\left(\frac{\partial \ln Q}{\partial T}\right)_{V} = \left(\frac{\partial \ln q'}{\partial T}\right)_{V}$$
$$\left(\frac{\partial \ln Q}{\partial T}\right)_{P} = \left(\frac{\partial \ln q'}{\partial T}\right)_{P} + \frac{1}{T}$$

then

But q' is independent of volume or pressure and its derivatives are equal in both expressions. Therefore, if

$$U - U_0 = RT^2 \left( \frac{\partial \ln Q}{\partial T} \right)_V = RT^2 \frac{d \ln q'}{dT}$$
 (5.47)

then, using the derivative at constant pressure, we get

$$RT^{2} \left( \frac{\partial \ln Q}{\partial T} \right)_{P} = RT^{2} \frac{d \ln q'}{dT} + RT$$
 (5.48)

But the first term on the right-hand side is equal to  $U - U_0$  and the second term RT = PV; therefore, on the basis of the preceding expression we obtain the enthalpy for a mole of an ideal gas:

$$H - H_0 = U - U_0 + PV = U - U_0 + RT = RT^2 \left(\frac{\partial \ln Q}{\partial T}\right)_P$$
 (5.49)

since evidently  $H_0 = U_0$  at T = 0.

Heat Capacity at Constant Volume. Heat capacity at constant volume is determined by the following well-known thermodynamic relation

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V \tag{5.50}$$

Hence, differentiating relation (5.46) with respect to temperature, we get directly

$$C_{V} = k \left[ 2T \left( \frac{\partial \ln \mathcal{F}}{\partial T} \right)_{V} + T^{2} \left( \frac{\partial^{2} \ln \mathcal{F}}{\partial T^{2}} \right)_{V} \right] = R \left[ 2T \left( \frac{\partial \ln Q}{\partial T} \right)_{V} + T^{2} \left( \frac{\partial^{2} \ln Q}{\partial T^{2}} \right)_{V} \right]$$

$$(5.51)$$

In this case too, the use of  $\mathcal{F}$  and Q leads to identical results. Entropy. As known, the change in the entropy of a system undergoing a change in an equilibrium process is equal to the reduced heat:

$$dS = \frac{\delta Q}{T} \tag{5.52}$$

At constant volume  $\delta Q = C_V dT$  and, hence, on the basis of Eq. (5.51),

$$S - S_0 = \int_0^T \frac{C_V}{T} dT = k \int_0^T \left[ 2 \left( \frac{\partial \ln \mathcal{F}}{\partial T} \right)_V + T \left( \frac{\partial^2 \ln \mathcal{F}}{\partial T^2} \right)_V \right] dT$$

The first integral is evidently taken directly and the second is determined by parts. The result is

$$S - S_0 = k \ln \mathcal{F} - k \ln \mathcal{F}_0 + kT \left(\frac{\partial \ln \mathcal{F}}{\partial T}\right)_V$$
 (5.53)

Further, by equating  $S_0$  to k In  $\mathcal{F}_0$  and thus introducing the statistical analog of the Planck postulate, we may write the relation

between the entropy and the grand partition function:

$$S = k \ln \mathcal{F} + kT \left( \frac{\partial \ln \mathcal{F}}{\partial T} \right)_{V} \tag{5.54}$$

But if we make use of the molecular partition function Q, then, according to Eq. (5.46), the expression will have a somewhat different form, namely:

$$S = R \ln \frac{Qe}{N_{\rm A}} + RT \left(\frac{\partial \ln Q}{\partial T}\right)_{V}$$
 (5.55)

Here  $N_A$  is the Avogadro number. As seen, formulas (5.54) and (5.55) are no longer identical.

The Helmholtz Free Energy. By definition, the Helmholtz free energy is equal to

$$F = U - TS$$

Substituting the expressions for the internal energy (5.46) and entropy (5.54), we get

$$F - U_0 = -kT \ln \mathcal{F} = -RT \ln \frac{Qe}{N_\Lambda}$$
 (5.56)

The Gibbs Free Energy. By definition, the Gibbs free energy is equal to

$$G = U - TS + PV = F + PV$$

or for a mole of an ideal gas, using Eq. (5.56), we find

$$G - H_0 = F - U_0 + RT = -kT \ln \mathcal{F} + RT = -RT \ln \frac{Q}{N_A}$$
 (5.57)

Perhaps, it should be noted that in all the formulas containing the gas constant R, for example, in (5.55), (5.56) and (5.57), the calculation is carried out per 1 mole, and also that at absolute zero the values of the thermodynamic functions are equal, i.e.,

$$U_0 = H_0 = F_0 = G_0$$

The Chemical Potential and the Equilibrium Constant. Passing over to the derivation of a statistical expression for the equilibrium constant of a chemical reaction, let us first consider an ideal-gas mixture containing  $N_1$  molecules of the first component,  $N_2$  molecules of the second component, etc. Since the collection of particles of each of the components may be presented as independently coexisting systems, subsystems, the grand partition function of the mixture should be written in the form of the product of the corresponding partition functions for the subsystems, i.e.,

$$\mathcal{F}_{\text{mixture}} = \mathcal{F}_1 \mathcal{F}_2 \mathcal{F}_3 \dots$$

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$$\ln \mathcal{F}_{\text{mixture}} = \sum_{i} \ln \mathcal{F}_{i} = \sum_{i} N_{i} \ln \frac{Q_{i}e}{N_{i}}$$
 (5.58)

which takes account of relation (5.46) between the grand ( $\mathcal{F}$ ) and molecular (Q) partition functions. The Helmholtz free energy for the gas mixture is written in the following form in accordance with Eq. (5.56):

$$(F - U_0)_{\text{mixture}} = F_{\text{mixture}} - \sum_{i} U_{0i \text{ (mixture)}} = -kT \ln \mathcal{F}_{\text{mixture}} =$$

$$= -kT \sum_{i} N_i \ln \frac{Q_i}{N_i}$$

where  $\sum U_{0i}$ , the sum of the zero energies of the components, is equal to the zero energy of the system. Further, differentiating  $F_{\text{mixture}}$  with respect to the number of molecules of a component, we take into account that the zero energy is an additive function and therefore the derivative of  $\sum U_{0i}$  with respect to  $N_i$  will give simply the zero energy of the component per molecule,  $\overline{U}_{0i}$ . Thus, the chemical potential of the *i*th component of the mixture will be expressed thus:

$$\bar{\mu}_{i} = \left(\frac{\partial F_{\text{mixture}}}{\partial N_{i}}\right)_{T, V, N_{i} \neq N_{i}} = -kT \ln \frac{Q_{i}}{N_{i}} + \overline{U}_{0i}$$

or, per mole,

$$\mu_{i} = N_{A} \,\bar{\mu}_{i} = -RT \, \ln \frac{Q_{i}}{N_{i}} + U_{0i} \tag{5.59}$$

where  $U_{0i}$  is the molar zero energy of the component.

Turning now to the chemical equilibrium, we first write the equation of the reaction in a general form:

$$v_1A_1 + v_2A_2 + \ldots \iff v_1'A_1' + v_2'A_2'$$

using the symbol  $A_i$  to denote the substances—the participants of the reaction, and expressing the number of moles through  $v_i$ .

From the thermodynamic theory of the chemical equilibrium we know the general condition to be

$$\sum_{i} v_{i} \mu_{i} = 0 \tag{5.60}$$

where the sum is also extended over the reactants and products. Substituting the expression for the chemical potential (5.59) into the equilibrium condition (5.60), we have:

$$RT \left\{ v_1' \ln \frac{Q_1'}{N_1'} + v_2' \ln \frac{Q_2'}{N_2'} + \dots - v_1 \ln \frac{Q_1}{N_1} - v_2 \ln \frac{Q_2}{N_2} - \dots \right\} = v_1' U_{01}' + v_2' U_{02}' + \dots - v_1 U_{01} - v_2 U_{02} - \dots = \Delta U_0$$
 (5.61)

where  $\Delta U_0$ , i.e., the algebraic sum of zero energies of the participants of the reaction, has the physical meaning of the heat effect of the reaction at absolute zero. This quantity is illustrated by Fig. 5.2 for the simplest reaction  $A \rightarrow B$ .

In what follows it will be useful to introduce a new function —

the partition function of the component per unit volume:

$$q_i = \frac{Q_i}{V} \tag{5.62}$$

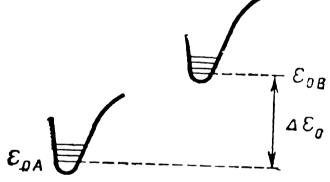
where V is the volume of the system. Using  $q_i$ , we now rewrite expression (5.61) in the following form:

$$\ln \frac{q_1^{\nu_1'} q_2^{\nu_2'} \dots \left(\frac{N_1}{V}\right)^{\nu_1} \left(\frac{N_2}{V}\right)^{\nu_1}}{q_1^{\nu_1} q_2^{\nu_2} \dots \left(\frac{N_1'}{V}\right)^{\nu_1'} \left(\frac{N_2'}{V}\right)^{\nu_2'}} = \frac{\Delta U_0}{RT}$$

Since the ratio  $N_i/V = C_i$  is the concentration of the given component expressed by the number of molecules per unit volume, the last relation turns readily into the following:

$$K_{C} = \frac{C_{1}^{\prime \nu_{1}^{\prime}} C_{2}^{\prime \nu_{2}^{\prime}}}{C_{1}^{\nu_{1}} C_{2}^{\nu_{2}}} = \frac{q_{1}^{\prime \nu_{1}^{\prime}} q_{2}^{\prime \nu_{2}^{\prime}}}{q_{1}^{\nu_{1}} q_{2}^{\nu_{2}}} e^{-\frac{\Delta U_{1}}{RT}}$$
(5.63)

And this is evidently the law of mass action written in the form of an ordinary equilibrium constant in terms of concentrations Fig. 5.2. The energy levels of the or in terms of the partition functions  $q_i$ . Writing the equilibrium



reactant and product.

constant in terms of partition functions is analogous to writing it in terms of concentrations, the term  $\exp\left(-\Delta U_0/RT\right)$  being added, which contains the heat of reaction at absolute zero,  $\Delta U_0 =$  $=\Delta E_0$ . For a theoretical calculation of the equilibrium constant by use of relation (5.63), apart from the value of  $\Delta U_0$ , it is necessary to know the various characteristics of the reacting molecules, i.e., the masses, vibrational frequencies, energy moments, symmetry numbers and electronic states.

The relation between the equilibrium constant and the partition functions per unit volume,  $q_i$ , determined by Eq. (5.62) and having the dimensions of concentrations, are also extensively used in the theory of chemical kinetics — the theory of absolute reaction rates.

It may also be noted that in expression (5.63) the heat of reaction may be referred not to a mole but to one molecule and instead of  $\Delta U_0/R$  or  $\Delta E_0/R$  we may write  $\Delta \varepsilon_0/k$ .

#### 5.8. Some Values of Level Degeneracy

We have already repeatedly written the molecular partition function in the most compact form, taking into account the multiplicity, or degeneracy, of the energy levels of molecules. Thus, Q is reduced to a form which takes account of the results of the application of quantum theory to the study of molecules. Namely,

$$Q = g_0 e^{-\frac{\varepsilon_0}{kT}} + g_1 e^{-\frac{\varepsilon_1}{kT}} + g_2 e^{-\frac{\varepsilon_2}{kT}} + \dots = \sum_i g_i e^{-\frac{\varepsilon_i}{kT}}$$
 (5.64)

where, as before, the summation is carried out over all the possible energy states of molecules. For monatomic molecules the degeneracy of levels is equal to the multiplicity of the corresponding spectral term \*. Thus, for atoms of inert gases in the ground electronic state  $g_0 = 1$  (the singlet level), and for atoms of alkali metals in the vapour state  $g_0 = 2$  (the doublet level). For molecules containing several atoms, the expression for g may become considerably complicated. Thus, for a diatomic molecule with a non-degenerate ground electronic level, the total degeneracy is determined by the degeneracy of the rotational level and is equal to

$$2J+1 \tag{5.65}$$

where J is the rotational quantum number. Since J may assume the values  $0, 1, 2, 3, \ldots$ , then only the ground level is non-degenerate. The other levels have degeneracies equal to 3, 5, 7, 9, etc.

In a complex molecule, there may also occur vibrational motions of atoms relative to their mean positions. We shall confine ourselves to the statement that the vibrational levels of all diatomic molecules are non-degenerate.

## 5.9. Approximate Values of the Partition Function of an Ideal Gas

In a general case, the energy of a molecule of an ideal gas may be represented by the sum of the translational energy, the electronic excitation energy, the vibrational energy, and the rotational energy, i.e.,

$$\varepsilon = \varepsilon_{\rm tr} + \varepsilon_{\rm el} + \varepsilon_{\rm vib} + \varepsilon_{\rm rot} \tag{5.66}$$

<sup>\*</sup> See the theory of origin of atomic and molecular spectra.

In the sum (5.66) the last three terms constitute the intramolecular energy and, strictly speaking, are interrelated—the vibration has an effect on the rotational energy, etc. The translational energy is specific in this respect—it is independent of the other types of motion and vice versa. Therefore, the total energy of the molecule can in all cases be split into two significantly different and independent components which refer to the translational motion and intramolecular states:

$$\varepsilon = \varepsilon_{\rm tr} + \varepsilon_{\rm intra} \tag{5.67}$$

Accordingly, the molecular partition function can also be represented in the form of two cofactors:

$$Q = Q_{\rm tr} Q_{\rm intra} \tag{5.68}$$

In the next section we shall describe a method of calculating the translational partition function  $(Q_{tr})$ . For the quantity  $Q_{intra}$  to be determined accurately, one must first of all have detailed information on the energy levels of the molecule, which is largely provided by spectroscopic methods of investigation. Second, one must undertake the painstaking task of summating terms of the type  $\exp(-\epsilon_i/kT)$  referring to individual energy levels. This method—the method of direct summation—is the only one reliable over a wide temperature range. However, it is laborious and is facilitated only by using electronic computers. Therefore, resort is often made to approximation methods which give satisfactory results at not too high temperatures. Thus, at a first approximation, it is believed that all the intramolecular forms of energy are also independent of one another. In such a case, the total molecular partition function may be represented as the product of the partition functions calculated for individual forms of energy, i.e.,

$$Q = Q_{\rm tr} Q_{\rm el} Q_{\rm vib} Q_{\rm rot} \tag{5.69}$$

We shall use only the formula of this approximation and therefore in the section that follows we shall be concerned with the determination of different  $Q_i$ 's separately.

# 5.10. The Simplest Partition Functions for Individual Types of Molecular Motion

The Energy of Electronic Excitation. Let a molecule have the following series of the lowest energy levels for the outer electron shell:  $\varepsilon_0 = 0$ ,  $\varepsilon_1$ ,  $\varepsilon_2$ , ... Here  $\varepsilon_0$  is the energy of the ground, unexcited level and is taken as the origin;  $\varepsilon_1$  and  $\varepsilon_2$  ... are, respectively, the energies of the urst, second, etc., excitation levels. The electronic partition function is written in a general form as

follows:

$$Q_{\rm el} = g_0 e^{-\frac{\varepsilon_+}{kT}} + g_1 e^{-\frac{\varepsilon_+}{kT}} + g_2 e^{-\frac{\varepsilon_+}{kT}}$$
(5.70)

where  $g_0, g_1$ ... are the multiplicities, or degeneracies, of the corresponding levels. In many cases, however, even the energy of the first electronic excitation level is high as compared with the average energy of thermal motion, a measure of which is kT. Thus,  $\varepsilon_1$  is often of the order of several (4-5) electron-volts; as for kT, this quantity is approximately equal to  $10^{-4}$  TeV; at room temperature (300 K) it will be equal to 0.03 electron-volt. Therefore, already in the second term the negative exponent may be much greater than unity and the term itself may be very small. Therefore, often at not too high temperatures all the terms in the partition function (5.70) may be neglected, except the first one, and the quantity  $Q_{e1}$  may be assumed to be equal to the degeneracy (multiplicity) of the ground electronic level, i.e.,

$$Q_{\rm el} = g_0 \tag{5.71}$$

This factor is usually included in the translational partition function which will be discussed below.

Translational Motion. In calculating the partition function for translation of an ideal gas, the molecule is regarded as a particle possessing only a mass and the ability to move in space.

The energy of unrestricted translational motion is not quantized in general, i.e., it may change continually—this kind of motion differs from the other types of motion which are periodic in character—vibration, rotation, etc. Therefore,  $Q_{\rm tr}$  should be calculated by means of integration rather than summation. And this is what we shall do. First of all, it must be shown that translational motion limited in its extent assumes, as it were, the properties of periodic motion, and its energy may take only certain discrete values.

Let us consider the simplest quantum-mechanical problem which is known as a particle in a potential box or, simply, as a particle in a box. Imagine a particle, say, a gas molecule, moving in a rectangular box of dimensions  $l_x$ ,  $l_y$ , and  $l_z$ . The properties of the particle-box system are such that the potential energy of the particle u(x, y, z) inside the box is constant and may be taken to be equal to zero. On the boundaries of the box, however, the potential energy of the particle is assumed to increase jumpwise to infinity, which means that the particle cannot actually go beyond the confines of the box.

In quantum mechanics, there is a postulate that the state of a microscopic system (an electron, an atom, a molecule) must

be defined by the Schrödinger wave equation:

$$\frac{h^2}{8\pi^2 m} \nabla^2 \psi + (E - u) \psi = 0 \tag{5.72}$$

In this equation  $\psi$  is the so-called wave function, the square of which \* expresses the density of the probability of finding a particle at a given point in space. The operator  $\nabla^2$  signifies the sum of the second partial derivatives of  $\psi$  in the coordinates x, y, and z, i.e.,

$$\nabla^2 \psi = \frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2}$$

Finally, m in Eq. (5.72) expresses the mass of the particle, and E and u denote, respectively, its total and potential energies. According to the formulated condition of the problem u=0. Let us consider a simplified solution of Eq. (5.72), assuming that the particle performs only a one-dimensional motion in the x direction from 0 to  $l_x$ . Then Eq. (5.72) becomes

$$\frac{h^2}{8\pi^2 m} \frac{d^2 \psi}{dx^2} + E_x \psi_x = 0 \tag{5.73}$$

The general solution of an equation of this type is known to be a sinusoidal function of the type

$$\psi_x = c \sin(Ax + B) \tag{5.74}$$

According to what has been said above,  $\psi_x^2$  will determine the probability of finding the particle at point x. From this it follows that  $\psi_x$  must be equal to zero at x=0 and at x=l, and this is possible only if

$$A = \frac{n_x \pi}{l_x}$$
 and  $B = 0$ 

where  $n_x$  is an integer, 1, 2, 3, .... Thus, the solution of Eq. (5.73) that satisfies all the conditions specified is

$$\psi_x = c \sin\left(\frac{n_x \pi}{l_x} x\right) \tag{5.75}$$

Substituting this solution into the original equation (5.69), we get

$$-\frac{h^2}{8\pi^2 m} \frac{n_x^2 \pi^2}{l_x^2} c \sin\left(\frac{n_x \pi}{l_x} x\right) + E_x c \sin\left(\frac{n_x \pi}{l_x} x\right) = 0$$

$$E_x = \frac{h^2}{8ml_x^2} n_x^2$$
(5.76)

or

<sup>\*</sup> More exactly, the product of complex-conjugate functions,  $\psi\psi^*$ .

where n is the quantum number which determines the allowable energy values for a particle constrained to move in the x direction only. According to Eq. (5.76),  $E_x$  may assume only those values which are multiples of  $h^2/8\pi l_x^2$ , and the restricted one-dimensional translational motion is found to be quantized. Figure 5.3 gives

 $\mathbf{F}_{x}$  m = 4 m = 3 m = 2 m = 1

Fig. 5.3. An approximate disposition of the energy levels of translational motion of particles [Eq. (5.76)].

a diagram of the energy levels  $E_x$  up to n = 4.

In general, it is precisely in this way that the discrete energy levels are obtained in more complex systems—in an electron interacting with the positively charged nucleus, in the vibrational motions of atoms in a molecule, and in the rotation of a molecule. As is known, the discrete nature of energy levels in an atom and molecule manifests itself in the pattern of spectra—emission, absorption and Raman spectra—etc. A detailed study of spectra provides information on the energy levels.

Returning to translational motion, we note that analogous solutions are obtained for the motion in the y and z directions, and by means of summation we could also write the total energy of the particle in the box. However, we shall not do this;

the box. However, we shall not do this; we shall only employ relation (5.76) for the direct calculation of the partition function for a one-dimensional translational motion:

$$Q_{\text{tr}(x)} = \sum_{n=1}^{\infty} e^{-\frac{h^2}{8ml_x^2kT} n_x^2}$$
 (5.77)

The calculation of this translational partition function is simplified because for gases the factor  $h^2/8ml_{\chi}^2kT$  is very small—the energy levels are closely spaced—and therefore, to a sufficient degree of approximation, the summation can be replaced by integration over n:

$$Q_{\text{tr}(x)} = \int_{0}^{\infty} e^{-\frac{h^{2}}{8ml_{x}^{2}kT}n_{x}^{2}} dn_{x} = \frac{(8mkT)^{1/2}}{h} l_{x} \int_{0}^{\infty} e^{-\beta^{2}} d\rho$$
 (5.78)

Here the following substitution is made:  $\rho^2 = h^2/8ml_x^2kT$ . The integral in Eq. (5.78) is known to be equal to  $\pi^{1/2}/2$ . Therefore we

obtain

or

$$Q_{\text{tr}(x)} = \frac{(2\pi mkT)^{1/2}}{h} l_x \tag{5.79}$$

Quite analogous results are obtained when calculating the partition functions for a motion parallel to the other two directions. Since the motions in all the three directions are independent, the total partition function for the translational motion of the particle in the box will be given by the product

$$Q_{\text{tr}} = Q_{\text{tr}(x)} Q_{\text{tr}(y)} Q_{\text{tr}(z)} = \frac{(2\pi mkT)^{3/2}}{h^3} l_x l_y l_z$$

$$Q_{\text{tr}} = \frac{(2\pi mkT)^{3/2}}{h^3} V$$
(5.80)

where V is obviously the volume of the box.

Formula (5.80) can be used to calculate the translational partition function for a gas molecule moving in an ordinary container. Let us, finally, combine, in accordance with what has been said above (page 134), the translational and electronic partition functions, i.e., the degeneracy of the ground electronic level:

$$Q_{\text{el. tr}} = g_0 \frac{(2\pi mkT)^{3/2}}{h^3} V$$
 (5.81)

In calculating the thermodynamic functions for  $N_{\Lambda}$  molecules, i. e., for one mole, the molar volume equal to RT/P for an ideal gas should be taken as V.

Vibrational Motion of Atoms in a Molecule (a Harmonic Oscillator). In diatomic molecules there arises a motion associated with the change of interatomic distances (bond lengths)—va-

lence vibrations (stretching or compression vibrations). In more complex molecules there are also possible various modes of deformation vibrations which lead to the change of bond angles. Let us consider in more detail the vibrations of atoms in a diatomic molecule.

Figure 5.4 (1) is a model of a diatomic molecule with an equilibrium distance between the nuclei,  $r_c$ ; it

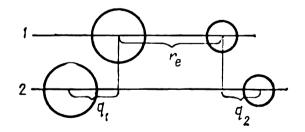


Fig. 5.4. The displacement of atoms in a diatomic molecule relative to the position of equilibrium.

shows the displacement of atoms (2) relative to the equilibrium position by the total amount  $q = q_1 + q_2$ . The restoring force arising during the displacement can be regarded, at a first approximation, as being proportional to the displacement or obeying Hooke's

law \*, i.e.,

$$F(q) = -K_c q$$

where  $K_c$  is the so-called force constant.

The potential energy is defined here by the parabolic displacement function:

$$u(q) = \frac{1}{2} K_c q^2 \tag{5.82}$$

The dependence of the potential energy of the molecule on displacement is given by the parabolic curve shown in Fig. 5.5 as a dashed line.

The solid line in Fig. 5.5 shows the actual dependence of the potential energy of the molecule on the distance between the

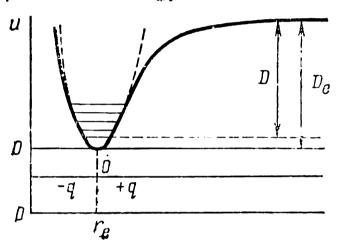


Fig 5.5. The potential energy of a molecule versus the interatomic distance:

 $D_e$ —spectroscopic energy of dissociation; D—chemical energy of dissociation of molecules.

atoms (interatomic distance) in the diatomic molecule. This curve is described by the Morse empirical function:

$$u = D_e [1 - e^{-a(r-r_e)}]^2$$

Its most significant difference from a parabola consists in that with increasing r the value of u tends to the limit equal to  $D_e$  (the spectroscopic dissociation energy). Obviously, the parabolic function is suitable, strictly speaking, only at small displacements. The motion of particles, which arises under vibration with a frequency

these conditions, is the harmonic vibration with a frequency

$$v = \frac{1}{2\pi} \sqrt{\frac{K_c}{\mu}}$$

where  $\mu = m_1 m_2/(m_1 + m_2)$  is called the reduced mass of the molecule. The instantaneous kinetic energy of vibrating atoms may be represented in the form

$$T = \frac{1}{2} \,\mu \dot{q}^2 \tag{5.83}$$

According to quantum theory, i.e., to the solution of the Schrödinger equation with these values of u and  $\mu$ , the energy of the harmonic oscillator vibrating with a frequency v is equal to

$$\varepsilon_{\text{vib}} = T + u = hv\left(v + \frac{1}{2}\right) \tag{5.84}$$

<sup>\*</sup> This force is therefore called the quasielastic force.

where v is the vibrational quantum number and may assume positive integer values;  $v = 0, 1, 2, 3, \ldots$ 

Figure 5.5 shows the equidistant levels of the total vibrational

energy of the molecule as a harmonic oscillator.

The partition function for the mode of vibration under discussion is written thus \*:

$$Q'_{\text{vib}} = \sum_{v=0}^{v=\infty} e^{-hv \left(v + \frac{1}{2}\right)/kT} = e^{\frac{hv}{2kT}} \left(1 + e^{-\frac{hv}{kT}} + e^{-\frac{2hv}{kT}} + \dots\right)$$
(5.85)

It is easy to see that enclosed in parenthesis is a series of geometric progression of the type

$$1 + x + x^2 + x^3 + \dots = (1 - x)^{-1}$$
 (5.86)

Therefore the vibrational partition function is given by

$$Q'_{\text{vib}} = e^{-\frac{h\nu}{2kT}} \left( 1 - e^{-\frac{h\nu}{kT}} \right)^{-1}$$
 (5.87)

The quantity hv/2 is the lowest value of the vibrational energy corresponding to v=0; this is the zero-point energy of the oscillator. It is often included in the total zero (i.e., at absolute zero) energy of the molecule and vibrational energy is usually measured from this lowest level (see page 127).

In this case the vibrational partition function assumes the following form

$$Q_{\text{vib}} = \left(1 - e^{-\frac{h\nu}{kT}}\right)^{-1} \tag{5.88}$$

From what has been said earlier it is clear that, strictly speaking, formula (5.88) is applicable only to a harmonically vibrating diatomic molecule, i.e., an ideal model which is never realizable in practice. As a matter of fact, with increasing q the potential energy tends not to infinity, as follows from Eq. (5.82), but to the limit  $D_c$  called the spectroscopic dissociation energy. The actual dependence  $u(q)_1 = f(q)$  is rather well described by the above-mentioned Morse empirical function which contains q in the exponent. Nevertheless, the results of the calculation of the partition function (5.88) differ little, especially at not too high temperatures, from those obtained by the more accurate method of direct summation over the approaching levels of anharmonic oscillators.

Calculation of the vibrational partition function for polyatomic molecules is an incomparably more formidable task. For this to

<sup>\*</sup> As pointed out earlier (p. 132), the vibrational levels of a diatomic molecule are non-degenerate ( $g_i = 1$ ).

be done, use is often made in practice of the zeroth-approximation method, which yields satisfactory results for moderate temperatures. This method allows for the existence in a polyatomic molecule of several (sometimes, many) modes of harmonic vibration with different frequencies, the energy of each of them being expressed by a formula of the type (5.84). A non-linear molecule consisting of n atoms has 3n-6 modes of vibration. For a linear molecule, because of the number of vibrational degrees of freedom being decreased by unity, the number of modes of vibration is 3n-5. If there is a degree of freedom of internal rotation in a molecule (for example, of the methyl groups about the bond line in ethane), the number of vibrations falls down to 3n-7. In a general case, when the number of modes of vibration is 3n-x, the partition function is approximately written in the following way:

$$Q_{\text{vib}} \approx \prod_{i=1}^{3n-x} \left(1 - e^{-\frac{hv_i}{kT}}\right)^{-1}$$
 (5.89)

Here the derivative contains analogous factors for all modes of vibration.

Rotation of a Molecule (a Rigid Rotator). According to quantum-mechanical calculations, the rotational energy of a diatomic molecule with the distance between the nuclei,  $r_c$ , being unchanged (the simplest model is the rigid rotator), is expressed by the relation

$$\varepsilon_{\text{rot}} = \frac{h^2}{8\pi^2 I} J (J+1) \tag{5.90}$$

where I is the moment of inertia, i.e.,

$$I = r_e^2 \frac{m_1 m_2}{m_1 + m_2} = r_e^2 \mu \tag{5.91}$$

and J is the rotational quantum number which assumes the values 0, 1, 2, 3, .... To each level of rotational energy (the value of the number J) there corresponds the degeneracy 2J+1. Therefore the partition function for rotation is given by

$$Q'_{\text{rot}} = \sum_{0}^{\infty} (2J+1) e^{-\frac{h'J(J+1)}{8\pi^{2}IkT}} = \sum_{0}^{\infty} (2J+1) e^{-\rho J(J+1)}$$
 (5.92)

Frequently, in the case of sufficiently heavy molecules and not too low temperatures, that is, when  $\rho$  is small, the direct summation is replaced by integration. If Z is substituted for  $J+\frac{1}{2}$ , then

2J + 1 = 2Z, and  $J(J + 1) = Z^2 - \frac{1}{4} \approx Z^2$ , and so

$$Q'_{\rm rot} \approx \int_{0}^{\infty} 2Z e^{-\rho Z^2} dZ$$

The integral is equal to  $1/\rho$ . Hence, the partition function

$$Q'_{\rm rot} = \frac{8\pi^2 I k T}{h^2} \tag{5.93}$$

Expression (5.93), however, is not complete. Usually, it also contains factors corresponding to the nuclear spin degeneracy (the spin factor).

A distinction is made between molecules having identical and different nuclei. The first form so-called *ortho-* and *para-*states. We shall examine this case in more detail. The spin quantum number of each nucleus is equal to i. Two identical spins are combined in 2i+1 ways; the resultant nuclear spin of the molecule may assume the following values:

$$2i$$
,  $2i - 1$ ,  $2i - 2$ ,  $2i - 3$ , ...,  $2$ ,  $1$ ,  $0$ 

The first, third, fifth, etc., values correspond in quantum mechanics to the symmetric fundamental functions or symmetric states. The second, fourth, sixth, etc., values correspond to the antisymmetric states. The general expression for the resultant spin is

$$t = 2i - n \tag{5.94}$$

where the lowest value of n is 0 and the highest value is 2i. The symmetric states (n is even or 0) are also called *ortho*-states. The antisymmetric states (n is odd) are termed *para*-states. For each value of the resultant spin, t, there are possible 2t + 1 orientations. Since t = 2i - n the degeneracy, i.e., the number of levels of equal energy corresponding to a combination of two nuclear spins, is 2(2i - n) + 1.

Thus, the total degeneracy of ortho-states will be given by

$$g_{\text{nuc (ortho)}} = \sum_{n=0, 2, 4, \dots, 2i} [2(2i-n)+1] = (i+1)(2i+1)$$
 (5.95)

and for para-states

$$g_{\text{nuc }(para)} = \sum_{n=1, 3, 5, \dots, 2i-1} [2(2i-n)+1] = i(2i+1)$$
 (5.96)

In writing the total rotational partition function for a molecule with identical nuclei it is necessary to know what values of rotational quantum numbers (even or odd) correspond to *orthoand para*-states. The problem is solved, for example, by experiment through a study of band spectra. The summation must be

carried out separately for ortho- and para-states. We get

$$Q_{\text{rot}} = g'_{\text{nuc}} \sum_{0, 2...} (2J+1) e^{-\rho J (J+1)} + g''_{\text{nuc}} \sum_{1, 3...} (2J+1) e^{-\rho J (J+1)}$$
 (5.97)

where  $g'_{\text{nuc}}$  and  $g''_{\text{nuc}}$  are determined by means of relations (5.95) and (5.96). Suppose that, as before,  $\rho$  is small. Then, the summation in Eq. (5.97) may be replaced by integration and it can be shown that each sum is equal to  $^{1}/_{2}\rho$ \*.

Hence,

$$Q_{\text{rot}} = \left(g'_{\text{nuc}} + g''_{\text{nuc}}\right) \frac{1}{2\rho} \tag{5.98}$$

But, according to Eqs. (5.95) and (5.96),  $g'_{\text{nuc}} + g''_{\text{nuc}} = (2i + 1)^2$ . Thus, the rotational partition function for a symmetrical molecule can be written thus:

$$Q_{\rm rot} = (2i+1)^2 \frac{8\pi^2 I k T}{2h^2} \tag{5.99}$$

In an unsymmetrical molecule, i.e., a molecule consisting of different nuclei, no *ortho*- and *para*-states are present. If the nuclear spins are equal to i and i', then, taking into account the number of possible orientations for each of them, we get the spin factor equal to (2i + 1) (2i' + 1). The calculation of the partition function for rotation will not differ from the calculation of the partition function (5.93). Thus, for an unsymmetrical molecule we obtain

$$Q_{\text{rot}} = (2i+1)(2i'+1)\frac{8\pi^2 lkT}{h^2}$$
 (5.100)

Comparing Eqs. (5.99) and (5.100), we see that they differ, first of all, in the denominator  $(2h^2 \text{ and } h^2)$ . The number 2 is considered to express the symmetry of the molecule, i. e., the number of indistinguishable positions occupied by the molecule upon rotation by 360°. In a general form, the symmetry number is denoted by the letter  $\sigma$ . Now we may finally write the expression for the rotational partition function for a diatomic molecule:

$$Q_{\text{rot}} = (2i+1)(2i'+1)\frac{8\pi^2 I k T}{\sigma h^2} = g_{\text{nuc}} \frac{8\pi^2 I k T}{\sigma h^2}$$
 (5.101)

which is suitable equally well for symmetrical and unsymmetrical molecules. Apparently, for symmetrical molecules, i and i' are equal and Eq. (5.101) turns into Eq. (5.99), and for unsymmetrical molecules  $\sigma = 1$ , from which follows Eq. (5.100).

<sup>\*</sup> Each sum is twice as less as the partition function (5.92) which equals  $1/\rho$  since here the summation is carried out over the levels.

Polyatomic Molecules. The rotational partition function for a non-linear polyatomic molecule having three identical moments of inertia (for example, methane or its symmetrical substituted derivatives) may be given by

$$Q_{\text{rot}} = g_{\text{nuc}} \frac{\pi^{1/2}}{\sigma} \left( \frac{8\pi^2 I k T}{h^2} \right)^{1/2}$$
 (5.102)

The spin factor is determined here by multiplying terms of the type (2i+1) through for each nucleus, and the symmetry number is  $\sigma = 12$ .

More often are examples of molecules in which two of the three moments of inertia are equal. Here we can obtain only an approximate expression for the partition function. Namely,

$$Q_{\text{rot}} = g_{\text{nuc}} \frac{\pi^{1/2}}{\sigma} \left( \frac{8\pi^2 kT}{h^2} \right)^{3/2} I_{\Lambda} I_{C}^{1/2}$$
 (5.103)

Analogously, we can write the partition function for a molecule having three different moments of inertia:

$$Q_{\text{rot}} = g_{\text{nuc}} \frac{\pi^{1/2}}{\sigma} \left( \frac{8\pi^2 kT}{h^2} \right)^{3/2} (I_{\Lambda} I_{\text{B}} I_{\text{C}})^{1/2}$$
 (5.104)

Thus, for the partition function to be evaluated by means of formula (5.104), there is no need to know the individual values of moments of inertia since there have been worked out methods for direct determination of the product  $(I_{\Lambda}I_{B}I_{C})$ .

In conclusion, it may be added that in calculations of the equilibrium constants and thermodynamic functions for these purposes the spin factor  $g_{\text{nuc}}$  in Eqs. (5.101) and (5.102), and in (5.103) and (5.104) may be dropped out since the nuclear state does not change in a chemical reaction in the absence of *ortho-para* conversions.

Internal Rotation: Free and Retarded Rotations. As has already been mentioned, a molecule can exhibit one more kind of motion—the rotation of one part of the molecule relative to the other, say, the rotation of methyl groups in the ethane molecule about the A—A axis passing through the carbon atoms:

$$\begin{array}{c} H \\ A - - - H - C \\ \hline \begin{pmatrix} f \\ f \end{pmatrix} C - H - - \Lambda \end{array}$$

The methyl groups may be regarded as symmetrical tops having two equal moments of inertia relative to the axes perpendicular to the principal axis of rotation of the top. Often in the mo-

lecule a rigid framework may be distinguished, to which one or more rigid tops are connected.

The possibility of internal rotation must be taken into account in setting up the total partition function since it reduces the number of rotational degrees of freedom. Sometimes the internal rotation may be regarded, at a first approximation, as a free rotation, i.e., a rotation not associated with the necessity of overcoming any energy barrier.

Let us introduce the so-called reduced moment of inertia:

$$I_m = \frac{I_1 I_2}{I_1 + I_2} \tag{5.105}$$

where  $I_1$  and  $I_2$  are moments of inertia relative to the axis of rotation of two parts of the molecule, which rotate one about the other. Then we can show that the partition function for internal rotation is evaluated by the relation

$$Q_{\rm fir} = \frac{(8\pi^3 I_m kT)^{1/2}}{h} \tag{5.106}$$

Here, however, no account is taken of the symmetry of the molecule. This can be done in two ways. First, the total symmetry number is inserted into the expression for the rotational partition function derived for external rotation [for example, into formula (5.104)]. In another method, the symmetry number is split into two parts: one for the external rotation of the rigid molecule exhibiting no internal rotation; the other component refers only to groups rotating inside the molecule. The second method is employed more frequently. So, the partition function for each freely rotating group is written thus:

$$Q_{fir} = \frac{(8\pi^3/kT)^{1/2}}{\sigma_i h}$$
 (5.107)

For instance, for ethane the total symmetry number is 18 and it may be included in the expression for the rotational partition function of the molecule as a whole. In the second method, however, this number, 18, is regarded as the sum of two cofactors. One of them, which is equal to 6, characterizes the rotation of the molecule as a whole: upon rotation about the C—C axis the molecule occupies three indistinguishable positions, each of which can be realized twice upon rotation by  $360^{\circ}$  about the axis perpendicular to the C—C bond. So,  $\sigma = 6$ . The symmetry number (or symmetry factor) for the internal rotation  $\sigma = 3$  since upon rotation of the methyl group about the C—C axis, as shown on page 143, it will also occupy three indistinguishable positions. Since the indistinguishable positions may combine in any way, there will be 18 such positions.

In a general case, a molecule can have S degrees of freedom of rotational motion: three of them refer to external rotation and S-3 degrees of freedom refer to internal rotation. A rather laborious calculation, which is based on the classical method and which includes integration over S coordinates and S momenta, gives a result which may be represented in the following form:

$$Q_{\text{rot}} = \left\{ \frac{\pi^{1/2}}{\sigma_e} \left( \frac{8\pi^2 kT}{h^2} \right)^{3/2} \left( I_{\text{A}} I_{\text{B}} I_{\text{C}} \right)^{1/2} \right\} \cdot \left\{ \prod_{l=1}^{S-3} \frac{(8\pi^3 I_k kT)^{1/2}}{\sigma_l h} \right\}$$
(5.108)

In this expression  $I_k$ 's are moments of inertia of S-3 groups which are considered to be freely rotating inside the molecule about the bonds linking these groups to the rigid framework of the molecule;  $\sigma_e$  is the symmetry number of external rotation;  $\sigma_l$  is the symmetry number of internal modes of rotation.

As can easily be seen, in the above formula the first term in braces coincides, within the nuclear spin factor absent from Eq. (5.108), with formula (5.104) which expresses the partition function only for the external rotation of a non-linear molecule with three different moments of inertia.

The second term in braces covers the product of S-3 cofactors which are analogous to those in Eq. (5.107) and correspond to S-3 degrees of freedom of internal rotation. According to the result obtained at a first approximation, the external rotation can be separated from the internal rotation and the latter can also be represented in the form of cofactors corresponding to the rotation of individual groups. Formula (5.108) can also be written in the following abbreviated form:

$$Q_{\rm rot} = Q_{\rm ex} \prod_{i=1}^{S-3} Q_{\rm fir}$$
 (5.109)

The difference between  $I_m$  in formula (5.106) and  $I_k$  in (5.108) should be noted. The first quantity denotes the reduced moment of inertia, and the second, the inertial moments of individual rotating groups.

Free internal rotation in pure form is encountered rather seldom. One of the few examples is the rotation of the methyl groups in dimethylcadmium, H<sub>3</sub>C—Cd—CH<sub>3</sub>. Here the rotating groups are separated by a relatively large distance—by two Cd—C distances instead of one C—C distance in ethane. The numerical data given below confirm the absence of hindered rotation. The agreement between the entropy calculated statistically and that determined experimentally on the basis of colorimetric data is very good, as can be seen from the data given.

### The entropy of dimethylcadmium as an example of the contribution of free internal rotation, cal/deg·mole

Translational motion and total rotation Vibrations			8.76
Total entropy as calculated	iaw		$72.35$ $72.40\pm0.20$

Hindered Rotation. The entropy value calculated on the assumption of free rotation in the molecules of ethane, propane, butane,

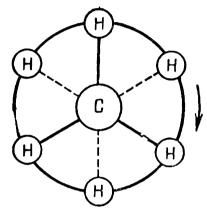


Fig. 5.6. The rotation of the methyl groups in ethane; the position of hydrogen atoms corresponds to the minimum of the potential energy of the molecule.

tetramethylmethane, etc., has been found to be somewhat higher than that found on the basis of colorimetric measurements. This has led to the belief that the rotation is not quite free; a certain energy barrier has to be surmounted—in the cases listed above the energy barrier to rotation is not high (2-3 kcal/mole).

The essence of the matter can most simply be ascertained by reference to the bipyramidal ethane molecule. Rotation is thought to be retarded due to the repulsion between the hydrogen atoms of the separate methyl groups. This force of repulsion attains a maximum when the hydrogen atoms in the separate methyl groups are opposite to each other, and a minimum when one group

rotates relative to the other at an angle of  $\pi/3$  (Fig. 5.6). The maximum value is again reached on rotation by another  $(1/3)\pi$  angle. The symmetry of the groups requires that identical maxima alternate with identical minima on rotation by 360°. The potential function can be expanded into a Fourier series but, as has been found, the first two terms give a quite good approximation. So

$$u = C_0 + C_1 \cos n\varphi + \dots = \frac{1}{2} u_0 (1 - \cos n\varphi) = u_0 \sin^2 (n\varphi/2)$$
 (5.110)

On the right-hand side of the above equation the potential is represented in the form which assumes its equality to zero at  $\varphi = 0$ . The quantity  $u_0$  evidently denotes the largest value of the potential and n is the number of equivalent positions on rotation of the group by 360°. If all n positions are quite equivalent, then n coincides with the symmetry factor and the potential may be represented in the following form:

$$u = u_0 \left(1 - \cos \sigma \varphi\right) \tag{5.111}$$

Figure 5.7 shows this dependence graphically for ethane. It is seen that, in accordance with  $\sigma_i = 3$ , identical maxima and minima alternate through every  $(^2/_3)\pi$ . Equation (5.110) can be exploited for the solution of the quantum-mechanical problem by means of Schrödinger's equation. In this case, however, no sufficiently simple expression is obtained for energy levels and the calculation of the partition function is complicated.

A general treatment of the problem is beyond the scope of the present book. We shall confine ourselves to the statement that, as

has been shown by Pitzer, the contribution of internal rotation u to the thermodynamic functions may be collected, in the form of two properly chosen variables, in summary tables. Thus, the variables that may be used are the ratio of the height of the potential barrier to the energy of thermal motion, i.e.,  $u_0/kT$ , and the inverse of the partition function for rotation which is considered free,  $1/Q_{\rm fir}$  \*. Such tables can also be em-

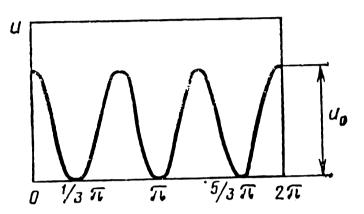


Fig. 5.7. The potential energy of the molecule on the angle of rotation of the methyl group in ethane.

ployed for the solution of the converse problem: if we know the contribution of retarded internal rotation to the total rotation, say the entropy, we can find the height of the potential barrier u.

## 5.11. Calculation of the Entropy of Monatomic and Diatomic Gases

As an example of the use of the formulas of statistical thermodynamics derived in the preceding sections, let us consider the calculation of the entropy of a diatomic gas. It should be noted here that, in accordance with the decomposition of the total partition function into cofactors, by relation (5.69), the thermodynamic functions may be represented as resolved into the corresponding components. For example, the entropy

$$S = S_{\text{el. tr}} + S_{\text{vib}} + S_{\text{rot}}$$
 (5.112)

Now, in accord with formula (5.54) we determine the molar entropy of an ideal diatomic gas. First, using Eq. (5.81), we find

<sup>\*</sup> Tables for heat capacity, enthalpy, the Gibbs free energy, and entropy can be found in: G. N. Lewis and M. Randall, *Thermodynamics*, McGraw-Hill Book Company, 1961.

the electronic-translational component  $S_{el.\ tr}$ :

$$S_{\text{el. tr}} = R \left\{ \ln \frac{g_0 \left[ 2\pi \left( m_{\text{A}} + m_{\text{B}} \right) kT \right]^{3/2}}{h^3} \frac{kT}{P} + \frac{5}{2} \right\} =$$

$$= R \ln g_0 + \frac{3}{2} R \ln M + \frac{5}{2} R \ln T - R \ln P_{\text{atm}} - 2.314 \text{ cal/mole} \cdot \text{deg} \quad (5.113)$$

This formula may also be used to calculate the total entropy of a monatomic gas at moderate temperatures, i.e., of a gas without electronic excitation of molecules. It is known as the Sackur-Tetrode equation. Further, according to Eqs. (5.54) and (5.88),

$$S_{\text{vib}} = R \left\{ \frac{h\nu}{kT} \left( e^{\frac{h\nu}{kT}} - 1 \right)^{-1} - \ln\left(1 - e^{-\frac{h\nu}{kT}}\right) \right\}$$
 (5.114)

At moderate temperatures a quantum of vibrational energy is usually larger than kT; in this case, Eq. (5.114) can be simplified by neglecting  $\exp(-hv/kT)$  as compared with unity and by neglecting unity as compared with  $\exp(hv/kT)$ :

$$S_{\text{v1b}} = R\left(\frac{hv}{kT}\right)e^{-\frac{hv}{kT}} \tag{5.115}$$

Finally, in compliance with Eqs. (5.54) and (5.101), we get

$$S_{\text{rot}} = R \left\{ \ln \left( \frac{8\pi^2 / kT}{\sigma h^2} \right) + 1 \right\} = R \ln \frac{TT}{\sigma} + 177.676 \text{ cal/deg} \cdot \text{mole}$$

Let us calculate the entropy of nitrogen in the standard state at 1 atm and a temperature of 298.1 K: M=28,  $g_0=1$ , R=1.987 cal/mole·deg. Hence, according to Eq. (5.113),

$$S_{298~el.~tr}^{\circ} = 35.95~eu$$
 (entropy units)

Further, as can easily be seen, at the vibration frequency  $\omega_e = 2359.60 \text{ cm}^{-1}$  the vibrational component of entropy is found to be vanishingly small, i.e.,

$$S_{298 \text{ vib}}^{\circ} \approx 0$$

In connection with this calculation it should be noted that generally on vibrations which arise along stable bonds and which therefore possess high frequencies, the corresponding contributions to the total entropy at moderate temperatures are negligibly small. A large contribution is introduced by weak vibrations such as deformation vibrations resulting in a change of valence angles.

The moment of inertia of the nitrogen molecule is  $I = 13.81 \times 10^{-40} \text{ g} \cdot \text{cm}^2$ , and the symmetry factor  $\sigma = 2$ . Hence, by using formula (5.116) we can determine the rotational component:

$$S_{298 \text{ rot}}^{\circ} = 9.84 \text{ eu}$$

If we compare the calculated entropy terms, we can see that the greatest contribution to the total entropy is made by translational motion, the lower by rotation and the lowest by vibration.

The total entropy of nitrogen in the standard state is equal, according to calculations based on molecular constants, to

$$S_{298}^{\circ} = S_{\text{el. tr}} + S_{\text{vib}} + S_{\text{rot}} = 45.79 \text{ eu}$$

This value is in good agreement with the entropy value obtained colorimetrically:

$$S_{298}^{\circ} = 45.77 \text{ eu}$$

Such calculations lead one to conclude that in many cases the thermodynamic functions determined by means of statistical methods on the basis of molecular characteristics are more accurate than those found by means of colorimetric measurements. As regards high temperatures encountered, for example, in plasma jets, the statistical methods are the only ones possible. True, under these conditions, the approximation given by relation (5.69) is no longer applicable, and more accurate methods must be employed, say, the method of direct summation.

In kinetics, use is invariably made of the first-approximation

formulas given in this chapter.

### CHAPTER 6

## Elements of the Kinetic Theory of Gases

This chapter deals with the derivation and consideration of certain formulas of the kinetic theory of gases, which are required for the treatment of the basic theories of chemical kinetics. Their derivation is based on the Boltzmann distribution law (5.33), which may be written in the following form:

$$dN_{i} = NA'g_{i}e^{-\frac{\varepsilon_{i}}{kT}}$$

$$\tag{6.1}$$

which differs from the previous one in that the partition function is replaced in it by its inverse quantity A', and the finite number of molecules  $N_i$  possessing the energy  $\varepsilon_i$  is replaced by the infinitely small  $dN_i$  because of the actual continuity of the change of the energy of translational motion. In formula (6.1),  $g_i$  is the statistical weight (degeneracy) of a given energy state of the molecule. In the case of the continuously varying energy, it can be obtained by using the Heisenberg uncertainty principle, from which it follows that the lowest determinable value of the product of the increments of the coordinate dq and the associated momentum dp is determined by the condition

$$dq dp \gg h \tag{6.2}$$

where h is Planck's constant. Hence, the volume of an elementary cell of the phase space \* is assumed to be equal to  $h^f$  if f is the number of degrees of freedom of motion. We shall first examine one-dimensional motion.

## 6.1. Distribution of Molecules in One Velocity Component

Let the energy of translational motion of a particle in the x direction be  $\varepsilon_i = m\dot{x}^2/2$  and the "volume" of the elementary cell be h (one-dimensional motion). Hence, the statistical weight of

<sup>\*</sup> A multidimensional space of coordinates and momenta, in which the state of a molecule or a system of molecules is specified by the position of a point (the representative point) (see Chapter 5).

the given energy state of the molecule with coordinates between x and dx and velocities between  $\dot{x}$  and  $\dot{x} + d\dot{x}$  will be written in the form

$$g_i = \frac{m \, d\dot{x} \, dx}{h} \tag{6.3}$$

Thus, the fraction of molecules possessing the characteristics indicated will be defined by

$$\frac{dN}{N} = A' \frac{m \, d\dot{x} \, dx}{h} \, e^{-m\dot{x}^2/2kT} \tag{6.4}$$

The proportionality factor A in Eq. (6.4) can be determined by integrating over  $\dot{x}$  from  $-\infty$  to  $+\infty$  and over x from 0 to a, where a is the length of the interval on which the motion is considered. The integration over x gives directly the factor a and therefore

$$\frac{dN}{N} = \frac{A'am}{h} e^{-m\dot{x}^2/2kT} d\dot{x}$$
 (6.5)

Here the fraction dN/N differs from that in Eq. (6.4), though it is written in the same form: this is the fraction of molecules moving along the interval a (which may be one of the dimensions of a rectangular container) with velocities between  $\dot{x}$  and  $\dot{x} + d\dot{x}$ . Further, we integrate over the velocity:

$$\int \frac{dN}{N} = \frac{A'am}{h} \int_{-\infty}^{+\infty} e^{-m\dot{x}^2/2kT} dx = 1$$

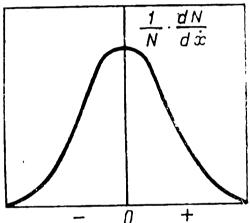


Fig. 6.1. The distribution of molecules in one velocity component x.

since the velocities of all the molecules are within the limits  $+\infty$  and  $-\infty$ . Integration \* of Eq. (6.5) leads to an expression for A':

$$A' = \frac{h}{(2\pi mkT)^{1/2} a} = \frac{1}{Q_{\text{tr}(1)}}$$
 (6.6)

where, incidentally,  $Q_{\rm tr(1)}$ , the inverse of A', is known as the partition function for one-dimensional translational motion \*\*. Substituting the value of A' obtained into Eq. (6.5), we get the following expression:

$$\frac{dN}{N} = \left(\frac{m}{2\pi kT}\right)^{1/2} e^{-m\dot{x}^2/2kT} d\dot{x}$$
 (6.7)

\* The integral 
$$\int_{-\infty}^{+\infty} e^{-ag^2} dg = (\pi/a)^{1/2}.$$

<sup>\*\*</sup> The quantity  $Q_{tr(1)}$  is derived by a different method and is considered in more detail in Chapter 5 (Sec. 5.10).

which is the distribution law for molecular velocities in one-dimensional motion. The ratio dN/N in Eq. (6.7) may be regarded as the probability that the velocity of a randomly chosen molecule will lie between  $\dot{x}$  and  $\dot{x} + d\dot{x}$ . Figure 6.1 is a graph of the function (6.7) in the form of the fraction of molecules, whose velocities are in the range  $\dot{x}$  to  $\dot{x} + 1$ . The most probable velocity is equal to zero and the fraction of molecules decreases symmetrically with increasing velocity in both directions. Before we proceed further, let us find, using the distribution law (6.7), the average velocity with which the molecules move in a single direction. It is found by summation of the absolute values of the velocity of all the molecules and by dividing the sum (integral) by the total number of molecules:

$$\bar{x} = \frac{\int \dot{x} \, dN}{N} = \left(\frac{m}{2\pi kT}\right)^{1/2} \int_{0}^{\infty} \dot{x} e^{-m\dot{x}^{2}/2kT} \, dx = \left(\frac{kT}{2\pi m}\right)^{1/2} \tag{6.8}$$

This expression will be of value at a later time.

### 6.2. Distribution of Molecular Velocities. The Maxwell Law

In three-dimensional motion the probability of a molecule having a velocity between  $\dot{x}$  and  $\dot{x}+d\dot{x}$ ,  $\dot{y}$  and  $\dot{y}+d\dot{y}$ , and  $\dot{z}$  and  $d\dot{z}$  will be expressed by the product of three equal probabilities of the type (6.7), i.e.,

$$\frac{dN}{N} = \left(\frac{m}{2\pi kT}\right)^{3/2} e^{-mc^2/2kT} d\dot{x} d\dot{y} d\dot{z}$$
 (6.9)

Here  $c^2 = \dot{x}^2 + \dot{y}^2 + \dot{z}^2$  is the total velocity of the molecule in the bulk. The above-indicated ranges of the velocity components restrict the velocity both in absolute value and in direction: the end of the radius-vector c must lie within the volume  $d\dot{x}\,d\dot{y}\,d\dot{z}$ . We are interested in the distribution of molecular velocities c rather than of their directions. Therefore, Eq. (6.9) must be integrated over all the possible directions. To do this, we pass from the rectangular coordinates to the spherical (polar) coordinates (Fig. 6.2), introducing the following variables: the length of the radius-vector c, the cone angle or colatitude 0, and the polar angle or longitude  $\Phi$ . As seen from Fig. 6.2, the element of the phase volume will be expressed with an accuracy of up to infinitely small values of the second order by the relation

$$d\dot{x} d\dot{y} d\dot{z} = c^2 dc \sin \theta d\theta d\Phi \tag{6.10}$$

Substitution into Eq. (6.9) and integration over the angle 0 between 0 and  $\pi$  and over the angle  $\Phi$  between 0 and  $2\pi$  gives the fraction of molecules, whose velocities are between c and c+dc, independently of the direction:

$$\frac{dN}{N} = 4\pi \left(\frac{m}{2\pi kT}\right)^{3/2} e^{-mc^2/2kT} c^2 dc \tag{6.11}$$

This is the Maxwell distribution law for molecular velocities. Figure 6.3 gives two curves showing the dependence of the fraction

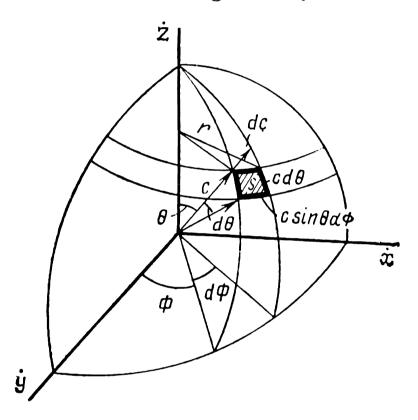


Fig. 6.2. Concerning the transformation of Cartesian coordinates to spherical coordinates:

Spherical coordinates: c—radius of sphere;  $\theta$ —latitude counted from the pole, and  $\Phi$ —longitude counted from the meridian passing through the y axis. The two closely spaced meridians and the two parallel circles form an area S on the surface of the sphere. The radius r of the parallel circle is equal to  $c\sin\theta$ , and one of the sides of the area rd  $\Phi=c\sin\theta d\Phi$ . The other side of the area is evidently equal to cd  $\theta$ . Because of the smallness of the area, we consider it to be rectangular: then  $S=c^2\sin\theta d\theta d\Phi$ . Now we increase the radius of the sphere from c to c+dc. With such an increase the area S will describe in space a parallelepiped of volume  $c^2dc\sin\theta d\theta d\Phi$ . It is this volume that is assumed to be equal (to an accuracy of infinitely small second order values) to a volume element in rectangular coordinates  $d\dot{x}d\dot{y}d\dot{z}$ . In order to take into account all the possible directions of the velocity, i. e., the radius c, it is necessary to change the latitude  $\theta$  from 0 to  $\pi$  and the longitude  $\Phi$  from 0 to  $2\pi$ .

of molecules having velocities between c and c+1 on c. As seen, the curves pass through a maximum which shifts to higher velocities with increase of temperature. This means that with rise of temperature the number of molecules moving with increased velocities increases. To the peak of the curve there corresponds the most probable velocity  $\alpha$ . Let us find the most probable velocity in an ordinary way, differentiating y = (1/N)(dN/dc) with respect

to c and setting the derivative equal to zero:

$$\alpha = \left(\frac{2kT}{m}\right)^{1/2} \tag{6.12}$$

The average velocity with which the molecules move at a given temperature is obtained if we multiply dN/N from Eq. (6.11) by c

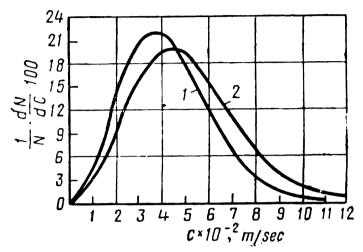


Fig. 6.3. The velocity distribution of oxygen molecules at two temperatures:

and integrate \* between zero and infinity:

$$\bar{c} = 4\pi \left(\frac{m}{2\pi kT}\right)^{1/2} \times$$

$$\times \int_{0}^{\infty} e^{-mc^{2}/2kT}c^{3} dc =$$

$$= \left(\frac{8kT}{\pi m}\right)^{1/2} = 1.128\alpha \quad (6.13)$$

The Root-Mean-Square Velocity. Let us first calculate the average square of the velocity,  $\bar{c}^2$ :

$$\bar{c}^2 = \frac{\int c^2 dN}{N} = 4\pi \left(\frac{m}{2\pi kT}\right)^{3/2} \int_0^\infty e^{-mc^2/2kT} c^4 dc \qquad (6.14)$$

Integrating \*\* Eq. (6.14), we get

$$\bar{c}^2 = \frac{3kT}{m} \tag{6.16}$$

\* The integral  $\int_{0}^{\infty} e^{-ag^2}g \, dg = 1/2a$  is elementary. If we differentiate it with

respect to a, we obtain directly  $\int_{0}^{\infty} e^{-ag^2} g^3 dg = \frac{1}{2} a^2.$ 

\*\* We proceed from the above-given integral (see footnote to page 151)

$$\int_{-\infty}^{+\infty} e^{-ag^{n}} dg = \left(\frac{\pi}{a}\right)^{1/2}$$

and differentiating it with respect to the parameter a, we obtain

$$\int_{-\infty}^{+\infty} g^2 e^{-ag^2} dg = \frac{\pi^{1/2}}{2a^{3/2}}$$

Now, taking the square root, we find the root-mean-square velocity:

$$u = \sqrt{\bar{c}^2} = \left(\frac{3kT}{m}\right)^{1/2} = \left(\frac{3}{2}\right)^{1/2} \alpha = 1.224\alpha \tag{6.17}$$

Thus, the average velocities obtained differ in magnitude and are arranged in the following sequence:  $u>c>\alpha$ . The root-mean-square velocity plays a very important part in the kinetic theory of gases since the gas pressure and the translational energy of the molecules of the gas are expressed in terms of  $u^2$ :

$$PV = RT = \frac{1}{3} N_0 m u^2, \quad E = \frac{1}{2} N_0 m u^2 = \frac{3}{2} RT$$
 (6.18)

The molar heat capacity of an ideal monatomic gas or a part of the heat capacity of a polyatomic gas, which refers to translational motion, will be obtained by differentiation of Eq. (6.18) with respect to temperature:

$$C_V = \left(\frac{\partial E}{\partial T}\right)_V = \frac{3}{2}R$$
 and  $C_P = C_V + R = \frac{5}{2}R$ 

## 6.3. The Number of Binary Collisions of Gas Molecules

Let us consider a mixture of gases consisting of molecules of types A and B; let the masses of the molecules be  $m_A$  and  $m_B$ . We first calculate the number of collisions of one molecule of type A with molecules of type B per second. What is meant here by the term collision? The main difficulty is that, strictly speaking, molecules have no definite dimensions since the density of electron clouds never becomes equal to zero. However, proceeding from this concept, it is impossible to calculate the number of collisions since the concept of collision itself cannot be defined either. Therefore, we make use of a crude model; molecules are likened to rigid spheres of various diameters. The diameters are determined by comparing the data of theoretical formulas with experimental measurements of the appropriate quantities (e.g.,

Differentiating once more with respect to a yields:

$$\int_{-\infty}^{+\infty} g^4 e^{-ag^2} dg = \frac{3\pi^{1/2}}{4a^{5/2}}$$

Now, from the symmetry considerations, we can write directly:

$$\int_{0}^{\infty} g^{4}e^{-ag^{2}} dg = \frac{3}{8} \frac{\pi^{1/2}}{a^{5/2}}$$
 (6.15).

the viscosity of a gas). In our case, the diameters of the molecules are assumed to be equal to  $D_A$  and  $D_B$ . A collision is defined here as an event involving the contact between two imaginable spheres. For the number of collisions of molecule A to be calculated, we imagine it moving in an arbitrary direction with an average relative velocity  $\bar{r}$ , the other molecule (B) is assumed to be immobile. A collision will take place if the centre of molecule B is at a distance not greater than

$$D_{AB} = \frac{D_A + D_B}{2}$$

from the line of motion of molecule A (Fig. 6.4). The total number of collisions of molecule A with molecule B per second can be found by multiplying the volume, described per second by

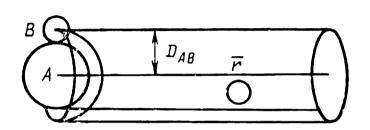


Fig. 6.4. Concerning the calculation of binary collisions.

a sphere of radius  $D_{AB}$ , by the number of molecules B in a unit volume  $(n_B)$ .

The volume is equal to  $\pi D_{AB}^2 \bar{r}$  and the number of collisions is

$$\pi D_{AB}^2 \bar{r} n_B \tag{6.19}$$

The average relative velocity of the molecules,  $\bar{r}$ , does not

coincide precisely with the average velocity  $\bar{c}$  of molecules of the same type calculated earlier. We shall not deal here with rather cumbersome calculations; for details the reader is referred to books on physical chemistry. The essence of the problem reduces to the following. The velocity with which a system consisting of molecules A and B is moving may be represented as two components:

- (1) the velocity of their common centre of mass (it is of no interest to us in this particular case);
- (2) the relative velocity, i.e., the velocity measured from the fixed centre of mass. The square of this velocity is equal to

$$r^2 = (x_A - x_B)^2 + (y_A - y_B)^2 + (z_A - z_B)^2$$

The average value of  $\bar{r}$  is calculated by means of a method reminiscent of the calculation of the average velocity  $\bar{c}$ . The result is found to resemble expression (6.13) for  $\bar{c}$ , the only difference being that the mass of one molecule, m, is replaced in the second case by the reduced mass of two molecules:

$$\mu = \frac{m_{\rm A} m_{\rm B}}{m_{\rm A} + m_{\rm B}} \tag{6.20}$$

Thus, the average relative velocity with which molecules A and B are moving is given by

 $\bar{r} = \left(\frac{8kT}{\pi\mu}\right)^{1/2} \tag{6.21}$ 

It should be noted that in the case of identical molecules  $m_A = m_B = m$  and

$$\mu = m/2$$
 and  $\bar{r} = 2^{1/2}\bar{c}$ 

Now, on the basis of Eqs. (6.19) and (6.21), we can finally arrive at the number of collisions of molecule A with molecules B per second:

$$D_{AB}^{2} \left\{ \frac{8\pi kT}{\mu} \right\}^{1/2} n_{B} = D_{AB}^{2} \left\{ 8\pi RT \left( \frac{1}{M_{\Lambda}} + \frac{1}{M_{B}} \right) \right\}^{1/2} n_{B} \sec^{-1} \text{ cm}^{-1}$$
 (6.22)

On the right-hand side of this equation the gram-molecular weights are introduced instead of the masses of the molecules and the Boltzmann constant is accordingly replaced by the gas constant R.

From relation (6.22) it follows that under standard conditions (1 atm and 298 K) the gas molecule experiences 10<sup>10</sup> collisions per second. The other conclusions made from Eq. (6.22) include, first of all, the definition of the *mean time between collisions* as the inverse of the number of collisions per molecule per second:

$$\tilde{\tau} = \frac{1}{D_{AB}^2 n_B} \left\{ \frac{\mu}{8\pi kT} \right\}^{1/2} \approx 10^{-10} \text{ sec (1 atm, 298 K)}$$
 (6.23)

and, second, the mean free path  $\lambda$ , i.e., the average distance traversed by molecule A between two collisions. The quantity  $\lambda$  is calculated by dividing the average velocity  $\bar{c}_{\Lambda}$  by  $\tau$ . Thus,

$$\lambda = \frac{\bar{c}_{\Lambda} \mu^{1/2}}{D_{\Lambda B}^{2} n_{B} (8\pi kT)^{1/2}}$$
 (6.24)

The average velocity is known from Eq. (6.13): it is equal to  $\bar{c} = (8kT/\pi m)^{1/2}$ . Further, we apply expression (6.24) to the case of molecule A colliding with like molecules. Then, as has already been shown, the reduced mass  $\mu = m/2$  and

$$\lambda = \frac{1}{2^{1/2} \pi D^2 n} = \frac{kT}{2^{1/2} \pi D^2 P}$$
 (6.25)

where the concentration of molecules n is expressed by the equation of state for an ideal gas, PV = NkT or P = nkT. Hence, at constant pressure  $\lambda$  is directly proportional to absolute temperature, which is a direct consequence of the decrease of the density of the gas, i.e., the increase of the average distance between the

molecules. Accordingly, at constant temperature  $\lambda$  is inversely proportional to the pressure for the same reason. At low pressures the mean free path may be comparable with the dimensions of the vessel containing the gas. For chemical reactions taking place under these conditions the walls of the containing vessel, at which the recombination of free atoms and radicals to form bond-saturated molecules occurs relatively easily, may become very important. It may be noted that at room temperature  $\lambda$  attains 20 cm at a pressure of about  $10^{-4}$  mm Hg.

We shall not consider this in detail; we merely point out that the mean free path is one of the quantities that determine the viscosity of a gas  $(\eta)$ . Namely,

$$\eta = \frac{1}{3} \, \bar{c} \rho \lambda \tag{6.26}$$

where  $\bar{c}$  is the average velocity of the molecules and  $\rho$  is the density of the gas. Experimental determinations of the viscosity allow us to find  $\lambda$  and, hence, the diameter of the molecule, D, using relation (6.25). This is one of the extensively used methods of determination of molecular diameters which are sometimes called gas-kinetic diameters. Other methods are based on measurements of heat conductivity, diffusion, and also on the determination of the constant b in the van der Waals equation of state.

Now we can find the number of binary collisions of molecules A with molecules B per unit volume (ml) per unit time (1 sec). To do this, we multiply the number of collisions per molecule A [relation (6.22)] by the number of such molecules in 1 ml. We get

$$Z_{AB} = D_{AB}^{2} \left\{ 8\pi RT \left( \frac{1}{M_{A}} + \frac{1}{M_{B}} \right) \right\}^{1/2} n_{A} n_{B} \frac{1}{\text{ml·sec}}$$
 (6.27)

Another important quantity in chemical kinetics is the total number of binary collisions of identical molecules. To calculate this quantity, we put  $M_A = M_B = M$  in formula (6.27) and introduce the factor 1/2 since without it we would count each collision twice. Thus,

$$Z = 2D^2 \left\{ \frac{\pi RT}{M} \right\}^{1/2} n^2 \tag{6.28}$$

# 6.4. The Number of Binary Collisions of Gas Molecules of Limited Energy with Energy Being Expressed by Two Quadratic Terms

For many problems of chemical kinetics to be solved, it will suffice to assume that the energy of colliding molecules is concentrated only in two degrees of freedom or, more exactly, is expressed by two quadratic terms. For example, when two mole-

cules collide, it suffices to take into account only the relative kinetic energy of motion along the line connecting their centres. This means, first of all, that molecular velocities are measured relative to the fixed centre of mass (relative velocities). Second, use is made not of the total relative velocities but only of their components along the centre lines; it is these velocity components that determine the speed with which the molecules approach one another. Denoting these components by  $v'_A$  and  $v'_B$ , we write the relative kinetic energy along the centre line in the following form:

$$R = \frac{m_{\rm A} (v_{\rm A}')^2}{2} + \frac{m_{\rm B} (v_{\rm B}')^2}{2}$$
 (6.29)

Let us calculate the number of collisions occurring at R equal to or greater than a certain critical value E, i.e., on the condition that  $R \gg E$ .

Consider two colliding molecules as a single system. Since we take into account only the motion along the line of the centres, we may assume that such a system has only two degrees of freedom, one per each molecule. In a more general case, as has already been mentioned, one speaks of the energy being expressed by two quadratic terms; an example is relation (6.29).

Thus, we may limit ourselves with the consideration of twodimensional motion and find the number of particles, i.e., pairs of colliding molecules possessing an energy not lower than Ein two degrees of freedom. We shall make use of the distribution law for one degree of freedom (6.7). With two degrees of freedom we shall examine the motion in the x and y directions. \* Just as in a more general case of motion in a three-dimensional space considered above, the corresponding distribution law is written as the product of two expressions similar to Eq. (6.7). Hence,

$$\frac{dN}{N} = \left(\frac{dN}{N}\right)_x \left(\frac{dN}{N}\right)_y = \frac{m}{2\pi kT} e^{-\frac{m(\dot{x}^2 + \dot{y}^2)}{2kT}} d\dot{x} d\dot{y}$$
 (6.30)

We introduce the symbol c for the two-dimensional velocity:

$$c^2 = \dot{x}^2 + \dot{y}^2$$

Thus, the expression

$$\frac{dN}{N} = \frac{m}{2\pi kT} e^{-\frac{mc^2}{2kT}} d\dot{x} d\dot{y} \tag{6.31}$$

is the fraction of particles for which the end of the velocity vector c will be within the confines of a rectangle of area  $d\dot{x} d\dot{y}$ 

<sup>\*</sup> Mathematically, this treatment is quite equivalent to the motion of two particles in a single direction.

(Fig. 6.5). As before, we must climinate velocity restrictions as to direction. To do this, we pass over, with the aid of Fig. 6.5, from the rectangular coordinates to the polar coordinates. Now the element of the phase volume (surface) will be given to

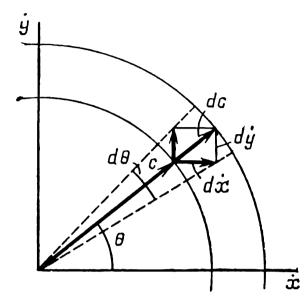


Fig. 6.5. The change to polar coordinates at two degrees of freedom.

within infinitely small values as follows:

$$d\dot{x} \, d\dot{y} = c \, d\theta \, dc \tag{6.32}$$

We rewrite Eq. (6.31), substituting Eq. (6.32):

$$\frac{dN}{N} = \frac{m}{2\pi kT} d\theta e^{-\frac{mc^2}{2kT}} c dc \quad (6.33)$$

and, integrating over  $\theta$  between 0 and  $2\pi$ , we eliminate velocity restrictions as to direction. We obtain

$$\frac{dN}{N} = \frac{m}{kT} e^{-\frac{mc^2}{2kT}} c dc \qquad (6.34)$$

Now the distribution law expresses the fraction of particles, whose two-dimensional velocity is in the range c to c+dc, irrespective of the direction. Note that by modifying the distribution laws we always express the fraction of particles by the ratio dN/N in order to avoid encumbering the text with new subscripts. As a matter of fact, the quantity dN/N in Eq. (6.33) is not equal to that in (6.34). In the second case, the fraction dN/N is obviously greater by many times.

We now pass over from velocity to translational energy &:

$$\varepsilon = mc^2/2$$
 and  $d\varepsilon = mc dc$  (6.35)

Substituting Eq. (6.35) into Eq. (6.34), we find the fraction of particles:

$$\frac{dN}{N} = \frac{1}{kT} e^{-\frac{\varepsilon}{kT}} d\varepsilon \tag{6.36}$$

whose energy is in the range  $\varepsilon$  to  $\varepsilon + d\varepsilon$ . Integration of Eq. (6.36) over  $\varepsilon$  between  $\varepsilon$  and infinity yields the fraction of molecules, whose energy is equal to or greater than  $\varepsilon$ :

$$\frac{N_{\varepsilon}}{N} = e^{-\frac{\varepsilon}{kT}}$$

OL

$$N_{e} = Ne^{-e/kT} \tag{6.37}$$

or \*

$$N_E = Ne^{-E/RT}$$

Note that first the resulting expression (6.37) is the only case in the kinetic theory of gases where the fraction of molecules is simply equal to the Boltzmann factor  $\exp(-\varepsilon/kT)$ ; second, and this is more important, expression (6.37), which is obtained for two translational degrees of freedom, retains, as can be shown, its validity for any case where the energy is expressed by two quadratic terms. For instance, the energy of harmonic vibration (for more details, see Sec. 5.10) may also be represented by two quadratic terms corresponding to the potential and kinetic energies:

$$\varepsilon_{\text{vib}} = u_{(q)} + T = \frac{1}{2} K_c q^2 + \frac{1}{2} \mu \dot{q}^2$$
 (6.38)

Here q is the shift from the equilibrium position,  $K_c$  is the force constant, and  $\mu$  is the mass equivalent. Therefore, relation (6.37) may also express the number of diatomic molecules,  $N_E$ , with a vibrational energy equal to or greater than E (ergs/mole, cal/mole). Likewise,  $N_E$  may be regarded as the number of colliding pairs of molecules, whose relative kinetic energy along the centre line is equal to or greater than E, of the total number  $Z_{AB}$  or Z [Eqs. (6.27) and (6.28)]. Using Eq. (6.37) for this case, we multiply Z or  $Z_{AB}$  by  $e^{-E/RT}$  to find the value of  $Z_E$ :

$$Z_E = Ze^{-\frac{E}{RT}} \tag{6.39}$$

which will give the number of binary collisions of molecules, which occur with an energy equal to or greater than E on the condition that the energy is expressed by two quadratic terms. Formula (6.39) plays an important part in chemical kinetics.

# 6.5. The Number of Binary Collisions with a Limited Energy Value when the Energy is Expressed by s Quadratic Terms

In solving certain problems of chemical kinetics the presence of two quadratic terms in the energy expression is found to be insufficient. For example, in addition to the relative kinetic energy along the line of the centres of colliding molecules, the energy of vibrational motions inside the molecules themselves must be taken into account. As has already been said [Eq. (6.38)], the

<sup>\*</sup> Here  $E = \varepsilon N_A$ , i.e., the energy is calculated per mole rather than per molecule; accordingly k is replaced by the gas constant  $R = kN_A$ .

energy of every mode (degree of freedom) of vibration may be expressed by two quadratic terms. If f vibrational degrees of freedom must be taken into account, s=2f+2 quadratic terms will then appear in the energy expression. The mathematical manipulations called for in connection with the deduction of the number of binary collisions (also called two-body collisions) with an energy equal to or greater than E and expressed by s quadratic terms are rather cumbersome and we shall not give them here. \* As a result, we get

$$Z_{E} = Z \left[ \frac{\left(\frac{E}{RT}\right)^{\frac{1}{2}s-1}}{\left(\frac{1}{2}s-1\right)!} + \frac{\left(\frac{E}{RT}\right)^{\frac{1}{2}s-2}}{\left(\frac{1}{2}s-2\right)!} + \dots + 1 \right] e^{-\frac{E}{RT}}$$
(6.40)

Equation (6.40) is ordinarily used in a simplified form, which is arrived at in the following way. If we divide, for example, the first term in square brackets by the second, the quotient

$$\frac{E}{RT\left(\frac{1}{2}s-1\right)}$$

will apparently be high if E is much greater than RT. Hence, on condition that

$$E \gg RT \tag{6.41}$$

the first term is much greater than the second. The same may be said about every other term of the sum as compared with the next one. Therefore, in view of condition (6.41) we may in general eliminate all the terms of the sum, except the first one. We then get

$$Z_{E} = Z \frac{\left(\frac{E}{RT}\right)^{\frac{1}{2}s-1}}{\left(\frac{1}{2}s-1\right)!} e^{-\frac{E}{RT}}$$
(6.42)

As can easily be seen, with two quadratic terms (s=2) formula (6.42) turns into formula (6.39). The most significant point in formula (6.42) is that with ordinary values of E/RT and s the additional factor may have a value of several orders of magnitude. This means an increase in the number of collisions of molecules having an energy equal to or greater than E, with an increase in the number of quadratic terms. The physical meaning

<sup>\*</sup> The derivation was first carried out by C. N. Hinshelwood (see C. N. Hinshelwood, Kinetics of Chemical Change, Clarendon Press, Oxford, 1940). See also E. A. Moelwyn-Hughes, Physical Chemistry, Pergamon Press, 1964.

of this increase is clear—it is easier for a molecule or molecules to accumulate energy E if the latter is distributed over a large number of degrees of freedom.

### 6.6. The Number of Triple Collisions

We have defined a binary collision as the contact between two rigid spheres representing a molecule. If it is assumed that such a collision occurs instantaneously, then reasoning in the same manner and defining the collision of three particles as the contact

of three spheres, we shall be faced with unresolvable problem since probability of a collision of three particles will be equal to zero. Thus, it is expedient, following Tolman, to reject the concept of a binary (or two-body) collision as the moment when the centre of the smaller molecule is on the surface of a sphere of radius  $D_{12}$  $=r_1+r_2$  (Fig. 6.6) and to assume that two molecules are in a "state of collision" as far as the centre of the smaller molecule is inside the spherical layer of radius  $D_{12}$  and  $D_{12} + \delta$ . The thickness of the layer  $\delta$  is arbitrary; we can only say that this thickness may evidently be of the order of 1 Å.

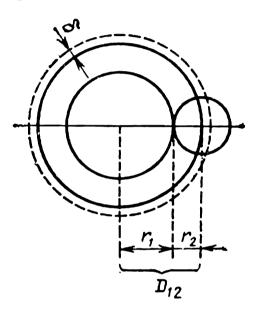


Fig. 6.6. Concerning the calculation of triple collisions

The average duration  $\tau$  of the thus defined binary collision can be shown to be equal to

$$\tau = \delta \left( \frac{2\pi\mu}{kT} \right)^{1/2} \tag{6.43}$$

The quantity, which is the reciprocal of  $\tau$ , is the probability of breakdown of the binary complex during 1 sec:

$$\frac{1}{\tau} = \frac{1}{\delta} \left( \frac{kT}{2\pi\mu} \right)^{1/2} \tag{6.44}$$

The volume of a spherical layer of thickness  $\delta$  (Fig. 6.6) is  $4\pi D_{12}^2 \delta$ . If the unit volume contains  $n_1$  large molecules of the first species, then the total volume of all the layers around them, which is equal to  $4\pi D_{12}^2 \delta n_1$ , will express the probability that the centre of the smaller molecule will be inside the layer, i.e., the probability of collisions. If the number of smaller molecules is  $n_2$ , then the number of simultaneously existing binary complexes,  $n_{12}$ , will be equal to

$$\mathbf{n}_{12} = 4\pi D_{12}^2 \, \delta n_1 n_2 \tag{6.45}$$

Reasoning in an analogous way, for the other pair we find that  $4\pi D_{23}^2$   $\delta n_3$  is the probability of a collision of the smaller molecule with a molecule of a third kind. Hence, we can find the number of triple complexes in 1 cm<sup>3</sup>:

$$n_{123} = 4\pi D_{12}^2 4\pi D_{23}^2 \delta^2 n_1 n_2 n_3 \tag{6.46}$$

The triplet ceases to exist when one of its constituent pairs is destroyed; the probability of the triplet being destroyed is equal to the sum of the probabilities of destruction of pairs, i.e., according to Eq. (6.44),

$$\frac{1}{\tau} = \frac{1}{\delta} \left( \frac{kT}{2\pi\mu_{12}} \right)^{1/2} + \frac{1}{\delta} \left( \frac{kT}{2\pi\mu_{23}} \right)^{1/2}$$
 (6.47)

In the state of equilibrium \* the number of triplets formed per unit time is equal to the number of complexes destroyed. This latter number is found by multiplying the number of triple complexes in 1 cm³, which is given by Eq. (6.46), by the probability of breakdown of the complex [Eq. (6.47)]; thus, we can immediately write the total number of collisions between molecules of three different species in 1 cm³ per 1 sec:

$$Z_{123} = 8 \sqrt{2} \pi^{1/2} D_{12}^2 D_{23}^2 \delta(kT)^{1/2} \left\{ \frac{1}{\mu_{12}^{1/2}} + \frac{1}{\mu_{23}^{1/2}} \right\} n_1 n_2 n_3$$
 (6.48)

The expression derived is employed in studying termolecular reactions. It is especially important that the number of triple collisions (also called ternary or three-body collisions) is proportional to the product of the concentrations of three types of colliding molecules. Of importance in kinetics is a triple collision of the type

$$2A + B \longrightarrow ...$$

In this case, only the concentration term in formula (6.48) will undergo a substantial change: instead of  $n_1n_2n_3$  there will appear the product  $n_1^2n_2$ . To the other cofactors there will be added an extra coefficient of minor importance.

### 6.7. The Frequency of Collisions of Molecules with the Wall

Let us determine the number Z of molecules colliding with a flat surface of area 1 cm<sup>2</sup> per second. Suppose, for example, that we have a rectangular area of indicated size chosen on the yz

<sup>\*</sup> Here the usual assumption is that the possible reaction between three molecules does not upset the equilibrium.

plane; if the average velocity in the x direction is  $\bar{x}$ , then, apparently, all the molecules inside the parallelepiped of height  $\bar{x}$  will strike the indicated area per second. With the concentration of molecules being equal to  $n \text{ cm}^{-3}$  the number of molecules in the volume of the parallelepiped is equal to  $n\bar{x}$ . Thus, the frequency of collisions of molecules with the wall will also be equal to  $n\bar{x}$ , i.e.,

$$Z = \overline{\dot{x}}n \tag{6.49}$$

The average velocity of molecules in a given direction has been calculated earlier [formula (6.8)].

Substitution of Eq. (6.8) into Eq. (6.49) gives

$$Z = n \left(\frac{kT}{2\pi m}\right)^{1/2} \tag{6.50}$$

If, finally, we make use of the equation of state for an ideal gas, p = nkT, the number of collisions of molecules per 1 sec per 1 cm<sup>2</sup> of flat surface can be given by

$$Z = \frac{P}{(2\pi mkT)^{1/2}} \tag{6.51}$$

This equation obtained by Hertz in 1882 is employed in the study of evaporation, condensation, and adsorption processes, heterogeneous chemical reactions, etc.

#### 6.8. Diffusion of Gases

Self-Diffusion. Suppose that, for some reason or other, the concentration in a gas becomes non-uniform. For example, along the z axis (Fig. 6.7) there occurs a concentration gradient dn/dz. Then, there arises a phenomenon called diffusion—the transport of a substance in the direction of the decrease of the gradient. Figure 6.7 shows three planes of area  $\Omega$  which are perpendicular to the z axis at a distance of the mean free path. The concentration is n at the ABCD plane,  $n + \lambda(dn/dz)$  at the upper plane, and  $n - \lambda(dn/dz)$  molecules/cm³ at the lower plane. If the average velocity of molecules in the z direction is  $\dot{z}$ , then the number of molecules crossing the ABCD plane per unit time will be  $\dot{z}\Omega[(n-\lambda dn/dz)]$  from bottom to top, and  $\dot{z}\Omega[(n+\lambda dn/dz)]$  from top to bottom.

The excess of substance transported upwards is given by According to Fick's empirical law, the same number is proportion-

$$\frac{dN}{dt} = -2\bar{z}\Omega\left(\frac{\partial n}{\partial z}\right)\lambda\tag{6.52}$$

al to the area of the interface and the concentration gradient

with a minus sign, i.e.,

$$\frac{dN}{dt} = -D\Omega \frac{dn}{dz} \tag{6.53}$$

where *D* is the diffusion coefficient.

Comparing expressions (6.52) and (6.53), we see that

$$D = 2\overline{\dot{z}}\lambda = \frac{1}{2}\,\bar{c}\lambda$$

Substituting into this expression the velocity of one-dimensional motion from formula (6.8) and the mean free path from

Eq. (6.25), we get an expression for the diffusion coefficient:  $\frac{1}{\sqrt{kT}} = \frac{kT}{\sqrt{kT}}$ 

$$D = \frac{1}{\pi \sigma^2 n} \left(\frac{kT}{\pi m}\right)^{1/2}$$
from which it is seen that at con-

from which it is seen that at constant pressure D is proportional to the temperature raised to the power 3/2, i.e., it does not depend on temperature very strongly. \* Here and afterwards, the gas-kinetic molecular diameters are designated as  $\sigma$  in contrast to the diffusion coefficient D. On the basis of Eq. (6.54) it is easy to show that even at low temperatures the so-called temperature

 $\begin{array}{c|c}
z \\
\hline
 & C \\
\hline
 & D \\
\hline
 & A \\
\hline
 & A$ 

Fig. 6.7. Concerning the calculation of the diffusion coefficient.

coefficient of diffusion (thermal diffusion coefficient)

$$\gamma_D = \frac{D_{T+10}}{D_T} \tag{6.55}$$

is close to unity. This conclusion is important for the study of the rate of heterogeneous chemical reactions: when the temperature coefficients of the reaction velocity are not much greater than unity, this is an indication, in most cases, that diffusion is the rate-determining step of the process. The diffusion coefficient can be determined by experiment and formula (6.54) can be used to find the molecular diameter, whose value coincides, within reasonable limits, with that found from viscosity by formula (6.26).

**Diffusion in Gas Mixtures.** Let us consider a mixture of two ideal gases with average concentrations  $n_1$  and  $n_2$  of molecules in 1 cm<sup>3</sup>. We assume that the gas pressure, which is proportional to  $n_1 + n_2$ , remains constant at all points. Therefore, the sum of

<sup>\*</sup> As compared with the exponential dependence of the reaction rate constant on temperature.

the possible concentration gradients for any direction is equal to zero, i.e.,

$$\frac{dn_1}{dz} + \frac{dn_2}{dz} = 0 \tag{6.56}$$

In the presence of concentration gradients there takes place the process of interdiffusion. In this process, the gas with a lower molecular weight will diffuse more rapidly in accordance with the greater D [formula (6.54)]. As a result, there may be developed a pressure difference, which is compensated for by the mass transport of the gas. Let this transport take place in the z direction with velocity  $v_0$ . Then the number of molecules crossing a plane of area 1 cm<sup>2</sup>, which is perpendicular to z, will be

$$\frac{dN_1}{dt} = v_0 n_1 - 2\overline{\dot{z}}_1 \lambda_1 \frac{dn_1}{dz} \tag{6.57}$$

and

$$\frac{dN_2}{dt} = v_0 n_2 - 2\overline{\dot{z}}_2 \lambda_2 \frac{dn_2}{dz} \tag{6.58}$$

By the condition of the constancy of pressure at all points in the system the total number of molecules crossing the plane in the given direction must be equal to zero, i.e.,

$$\frac{dN_1}{dt} + \frac{dN_2}{dt} = 0 \tag{6.59}$$

On the basis of Eqs. (6.57), (6.58), and (6.59) we find the speed of mass transport:

$$v_0 = \frac{2}{n_1 + n_2} \left\{ \overline{\dot{z}}_1 \lambda_1 \frac{dn_1}{dz} + \overline{\dot{z}}_2 \lambda_2 \frac{dn_2}{dz} \right\}$$
 (6.60)

In the discussion that follows it will be more convenient to replace the average velocity of unidimensional motion simply by the average velocity. According to Eqs. (6.8) and (6.13),  $\bar{z} = (1/4)c$ , and therefore

$$v_0 = \frac{1}{2(n_1 + n_2)} \left\{ \bar{c}_1 \lambda_1 \frac{dn_1}{dz} + \bar{c}_2 \lambda_2 \frac{dn_2}{dz} \right\}$$
 (6.61)

In the last equation the concentration gradients are equal [in accordance with Eq. (6.56)] in absolute value and opposite in sign. Taking the gradients, one at a time, out of the braces and substituting  $v_0$  into relations (6.57) and (6.58), we get, replacing  $\bar{z} = (1/4)c$ ,

$$\frac{dN_1}{dt} = -\left\{\frac{n_1\bar{c}_2\lambda_2 + n_2\bar{c}_1\lambda_1}{2(n_1 + n_2)}\right\}\frac{dn_1}{dz} \tag{6.62}$$

and

$$\frac{dN_2}{dt} = -\left\{\frac{n_1\bar{c}_2\lambda_2 + n_2\bar{c}_1\lambda_1}{2(n_1 + n_2)}\right\} \frac{dn_2}{dz}$$
(6.63)

It is obvious that the factors at the concentration gradients are identical and equal to the diffusion coefficient of each of the gases. Hence, the interdiffusion coefficient is given by

$$D_{1,2} = \frac{n_1 \bar{c}_2 \lambda_2 + n_2 \bar{c}_1 \lambda_1}{2 (n_1 + n_2)} = D_{2,1}$$
 (6.64)

In accordance with formula (6.24) the mean free path of a molecule of the first type in the second gas is defined by

$$\lambda_{1} = \frac{\bar{c}_{1}\mu^{1/2}}{\sigma_{12}n_{2}(8\pi kT)^{1/2}} = \frac{1}{\pi\sigma_{12}^{2}n_{2}(1 + m_{1}/m_{2})^{1/2}}$$

and the corresponding quantity for a molecule of the second type in the first gas is given by

$$\lambda_2 = \frac{1}{\pi \sigma_{12} n_1 \left(1 + m_2 / m_1\right)^{1/2}}$$

Substituting the mean free paths and average velocities into Eq. (6.64), we get an expression for the interdiffusion coefficient:

$$D_{1, 2} = \frac{1}{\pi \sigma_{12}^2 (n_1 + n_2)} \left( \frac{2kT}{\pi \mu} \right)^{1/2} = D_{2, 1}$$
 (6.65)

where

$$\mu = \frac{m_1 m_2}{m_1 + m_2}$$

expresses the reduced mass of the molecules.

In deriving formula (6.65) it was assumed that the diffusion is hindered only by collisions with molecules of another species since the collision with a molecule of the same type "forces" the molecule being struck farther and the diffusion is thus not retarded. Formula (6.65) is called the Stefan-Maxwell formula and is more consistent with experimental data than the formula derived from other assumptions. Similar formulas have been obtained by Langevin and Chapman.

# Simple Kinetic Theory of Activated Collisions

### 7.1. Bimolecular Reactions

The collision theory is based on the simple idea that for bimolecular reactions to take place, two molecules must collide, i.e., must approach close enough each other in order to react. Hence, the rate of the reaction, i.e., the number of molecules that react in unit volume per unit time, must be proportional to the number of collisions of the molecules (or to the number of colliding molecules) in the same volume for the same time.

Likening the molecules, at a first approximation, to elastic spheres and using, in this connection, formulas (6.27) and (6.28) for the number of collisions, we shall consider two cases.

1. Identical molecules collide and react; for example,

$$HI + HI \longrightarrow H_2 + I_2$$

Then the rate of the reaction will be

$$w = q2D^2 \left\{ \frac{\pi RT}{M} \right\}^{1/2} n^2 \frac{1}{\text{cm}^3 \cdot \text{sec}}$$
 (7.1)

where q is the proportionality factor, D is the molecular diameter, n is the concentration expressed by the number of molecules in 1 cm<sup>3</sup>, and M is the molecular weight.

2. Different molecules collide and react. For example,

$$H_2 + I_2 \longrightarrow 2HI$$

The reaction rate in this case is given by

$$\mathbf{w} = q' D_{AB}^2 \left\{ 8\pi RT \left( \frac{1}{M_A} + \frac{1}{M_B} \right) \right\}^{1/2} n_A n_B \frac{1}{\text{cm}^3 \cdot \text{sec}}$$
 (7.2)

From formulas (7.1) and (7.2) there directly follows an important conclusion: bimolecular reactions are second-order reactions (such reactions have been defined earlier). But, for the rate of the reaction to be calculated, it is necessary to know the proportionality factor q; it is very small, as can be shown. Let us consider, for this purpose, the reaction of decomposition of hydrogen

iodide at a temperature of 556 K and a concentration of 1 mole of HI in 22.4 litres \*. The molecular diameter is assumed to be equal to  $3.5 \times 10^{-8}$  cm. Hence, the number of colliding molecules

$$2z = 4D^{2} \left\{ \frac{\pi RT}{M} \right\}^{1/2} n^{2} = 4 \left( 3.5 \times 10^{-8} \right)^{2} \times \left\{ \frac{3.14 \times 8.3 \times 10^{7} \times 556}{127.9} \right\}^{1/2} \times \left( \frac{6.02 \times 10^{23}}{22,400} \right)^{2} \approx 1.2 \times 10^{29} \text{ cm}^{-3} \text{ sec}^{-1}$$

In order to find the number of actually reacting molecules we make use of the experimental value of the rate constant found by Bodenstein and equal to  $3.516 \times 10^{-4}$  cm<sup>3</sup>/mole·sec. Thus, the rate of the reaction is given by

$$w = k_{II} [HI]^2 = 3.516 \times 10^{-4} \left(\frac{1}{22,400}\right)^2 6.02 \times 10^{23} = 4 \times 10^{11} \text{ cm}^{-3} \text{sec}^{-1}$$

Now we can easily find the proportionality factor:

$$q_0 = \frac{4 \times 10^{11}}{1.2 \times 10^{29}} = 3.3 \times 10^{-18}$$

Such is the fraction of molecules (out of the total number of colliding molecules) that enter into reaction. Approximately the same can be expressed in a somewhat different manner. It has already been shown, with the aid of formula (6.23), that the average time between collisions,  $\tau$ , has a value of the order of  $10^{-10}$  sec under standard conditions (1 atm, 998 K). The half-life of molecules would be of the same order of magnitude if every collision were effective and resulted in reaction. In fact, it is usually greater by  $10^{15}$ - $10^{20}$  times.

Thus, not all collisions lead to reaction. Several causes may be indicated:

1. The necessity of an appropriate orientation of molecules at the moment of collision. Perhaps, more or less complex molecules can react if at the moment of impact they are properly oriented with respect to each other in space, i.e., if they form a configuration most suitable for the rupture of some bonds and the formation of new bonds. The fraction of collisions of appropriately oriented molecules is ordinarily estimated with the help of the steric or probability factor P. The values of P are less than unity. According to the data available, it may be expected that they have values ranging from those close to unity to 0.1-0.01-0.001, depending on the complexity of the reacting molecules. The theory of collisions does not provide a method of calculating the steric factor. It can be determined by comparing the calculated velocity with that found experimentally.

<sup>\*</sup> Such are the concentration units used by Bodenstein.

- 2. The necessity of stabilization of the molecule. As known from Chapter 2, for a bimolecular association of atoms or simple radicals, of the type  $H + H \rightarrow H_2$ , to be effected, a vibrationally excited molecule must be stabilized. The energy of excitation is at least equal to, and more often greater than, the energy required to break the bonds and therefore the quasi molecule formed exists only for one half-period of vibration, i.e., approximately for  $10^{-14}$  sec. What are the conceivable ways for the loss of excess energy? First, it is evident that this energy is intramolecular and cannot be transformed into the translational energy of the molecule as a whole according to the law of conservation of energy. In principle, the excess energy could be radiated in the form of a photon. \* However, in practice, evidently this path is excluded and the stabilization takes place by way of imparting the excess energy to a third body (see Sec. 2.3).
- 3. Quantum Interference Effects. If in a reacting system there must be changed the electronic state, say, the multiplicity, then the reaction will be slow, other conditions being equal. As an example of such reactions, called **non-adiabatic reactions**, we may cite some processes of *cis-trans* isomerization, in which the pre-exponential factor of the Arrhenius equation,  $Z'_0$  is only  $10^5$  sec<sup>-1</sup> or less (instead of the normal  $10^{13}$ ). It is possible that in such reactions the singlet ground state must turn into the triplet state, and the probabilities of such electronic transitions (forbidden transitions) are low. As other examples of non-adiabatic processes may be cited the processes of recharging of ions; for example,

$$M_1^- + M_2^+ \longrightarrow M_1 + M_2$$

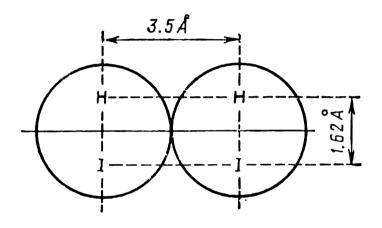
$$M_1 + M_2^{2+} \longrightarrow M_1^+ + M_2^+$$

4. Energy of Activation. A necessary condition for the effectiveness of a collision is the sufficient collision energy. The above-listed factors responsible for the decrease of the number of effective collisions operate in isolated cases. Since the time of Arrhenius, however, the energy condition has been thought to be the most important: an effective collision is primarily a collision in which molecules possess sufficient energy for them to be activated. The necessity of a sufficient energy, or even an excess energy, for an elementary reaction act to occur between bond-saturated

<sup>\*</sup> The shortest lifetime  $\tau$  of a vibrationally excited molecule with respect to the radiation process is observed in dipolar molecules. With a dipole moment of the order of  $10^{-18}$  e. s. u. the value of  $\tau$  is  $10^{-2}$  to  $10^{-3}$  sec. For molecules having no dipole moment,  $\tau$  is considerably greater, of the order of 1 sec. Since the vibrational frequency is about  $10^{+14}$  sec<sup>-1</sup>, the probability of a molecule of the type  $H_2$  (which has no dipole moment) being self-stabilized will be of the order of  $10^{-14}$ .

molecules may be demonstrated by the reaction  $2HI \rightarrow H_2 + I_2$ , which is a model reaction in our treatment.

Suppose that two molecules (spheres) of hydrogen iodide are brought into contact with each other (Fig. 7.1). The gas-kinetic diameter of HI is 3.5 Å. It is exactly this distance that separates the nuclei of the atoms  $H\cdots H$  and  $I\cdots I$ . But the internuclear distances in the reaction products are considerably smaller: 0.76 Å in  $H_2$  and 2.66 Å in  $I_2$ . In other words, the molecule HI must be considerably deformed during the collision for the corresponding atoms to be brought closer together and to give reaction products by forming new bonds. For such a deformation to occur, a considerable



 $v_A$   $v_B$   $v_B$ 

Fig. 7.1. An approximate distribution of atoms at the beginning of the collision of two molecules of hydrogen iodide.

Fig. 7.2. The velocity of molecules at the moment of collision.

erable amount of energy must be expended; this energy is known as the energy of activation.

From the standpoint of the collision theory the energy of activation may be defined as the minimum required energy that a molecule must possess at the moment of collision in order to react.

It is clear that the number of such activated collisions is much lower than the total number of collisions. To compute the number of activated collisions, it is necessary to establish what kind of energy is involved in the activation. Properly speaking, it is not the kind of energy itself but the number of quadratic terms in the energy expression that is important at the first stage of calculations. In the simplest variant of the collision theory of bimolecular reactions we are concerned with the relative kinetic energy of molecules along the line connecting their centres.

First, within the scope of the problem under consideration, it is reasonable to discount the total velocities of molecules moving, for example, relative to the walls of the vessel, and to place the origin of the coordinate system at the centre of the mass of the colliding system (at point O in Fig. 7.2). The velocities  $v_A$  and  $v_B$  as measured from point O may be called the relative velo-

cities (see also Sec. 6.4). However, it is not these velocities either that are important to the reaction, as one might think. The deformation of molecules, which is associated, so to say, with the "head-on force", will be determined by the projections of the vectors  $v_A$  and  $v_B$  onto the line joining the centres of the molecules, i.e., by the relative velocities along the line of the centre,  $v_A$  and  $v_B$ . The sum of the corresponding kinetic energies

$$R = \frac{m_{\rm A} \left(v_{\rm A}'\right)^2}{2} + \frac{m_{\rm B} \left(v_{\rm B}'\right)^2}{2}$$

is called the relative kinetic energy along the line of the centres. The condition for the efficiency of a collision, i.e., for a reaction to be accomplished, is the relation

$$R \equiv E$$
 (7.3)

where E is the critical value of energy, i.e., the energy of activation.

The problem of the number of binary collisions satisfying the condition (7.3)\* has been solved earlier (Sec. 6.4). Namely,

$$z_E = ze^{-E/RT}$$

or

$$\frac{z_E}{z} = e^{-E/RT} = q = q' \tag{7.4}$$

In the simplest version of the theory under consideration it is assumed that the rate of the reaction is equal to the number of activated collisions. Therefore, the ratio (7.4) determines the proportionality factors q and q' between the reaction rate and the total number of collisions in expressions (7.1) and (7.2). We rewrite them:

(1) for identical molecules

$$w = 2D^2 \left\{ \frac{\pi RT}{M} \right\}^{1/2} n^2 e^{-E/RT} \left( \text{cm}^{-3} \text{sec}^{-1} \right)$$
 (7.5)

(2) for different molecules

$$\mathbf{w} = D_{AB}^2 \left\{ 8\pi RT \left( \frac{1}{M_A} + \frac{1}{M_B} \right) \right\}^{1/2} n_A n_B e^{-E/RT} \left( \text{cm}^{-3} \text{sec}^{-1} \right)$$
 (7.6)

In what follows it is reasonable to pass from velocities to rate constants; first, we write

$$\mathbf{w} = k_{11}' \mathbf{n}^2 \tag{7.7}$$

<sup>\*</sup> The quantity  $z_E$  represents, in general, the number of collisions with an energy greater than E provided that this energy is expressed by any two quadratic terms of the type (6.29).

and

$$\boldsymbol{w} = k_{11}' n_{\Lambda} n_{\mathrm{B}} \tag{7.8}$$

Second, comparing expressions (7.5) and (7.7), and also (7.6) and (7.8), we get for like molecules:

$$k'_{II} = 2D^2 \left\{ \frac{\pi RT}{M} \right\}^{1/2} e^{-E/RT} = z_0 e^{-E/RT}$$
 (7.9)

if the reaction rate is determined with respect to one of the reaction products. Or

$$k'_{II} = 4D^2 \left\{ \frac{\pi RT}{M} \right\}^{1/2} e^{-E/kT} = z_0 e^{-E/RT}$$
 (7.10)

if the decrease of the number of reactant molecules is to be determined.

For unlike molecules we evidently get

$$k'_{II} = D_{AB}^2 \left\{ 8\pi RT \left( \frac{1}{M_A} + \frac{1}{M_B} \right) \right\}^{1/2} e^{-E_L kT} = z_0 e^{-E/RT}$$
 (7.11)

On the basis of Eqs. (7.9) and (7.11) we can write a general theoretical expression for the rate constant of a bimolecular reaction:

$$k'_{II} = z_0 e^{-E/RT} \tag{7.12}$$

in which  $z_0$  is the number of collisions at a concentration of molecules equal to unity ( $z_0$  is known as the standard collision frequency), and E is called the true energy of activation, in distinction to the experimental, apparent or Arrhenius energy of activation,  $E_A$ , from formulas (4.11) and (4.15). As will be shown,  $E_A$  differs from  $E_A$ . On the whole we may still assert that the theoretical equation (7.12) is closely reminiscent, in its form, of the Arrhenius equation (4.15) and allows the rate constant to be expressed in terms of two cofactors: the pre-exponential factor  $z_0$ , which is but slightly dependent on temperature ( $\sim T^{1/2}$ ), and the term  $\exp(-E/RT)$  which is what defines the principal dependence of  $k_{11}$  on T. The coincidence of the forms of functions (4.15) and (7.12) may undoubtedly be regarded as a success of the theory developed independently by Trautz (1916) and Lewis (1918).\*

The theory under discussion provides no methods for theoretical calculation of the energy of activation, therefore when this theory is compared quantitatively with experiment we have to compare only the easily calculable pre-exponential factors or to

<sup>\*</sup> Trautz published his work in Germany and Lewis, in the USA during the World War I when there was no exchange of information between the two countries.

make use of the experimental energy of activation for the calculation of the rate constant.

Let us return to the reaction of decomposition of hydrogen iodide. We shall still assume that  $E=E_{\Lambda}=44,560$  cal/mole and calculate the coefficient q for the temperature 556 K:

$$q = e^{-44,560/R \cdot .556} = 10^{-0.4343 \cdot 11.569/1112} = 10^{-18.23} = 1.7 \times 10^{-18}$$

This calculation is not exact since it makes direct use of the experimental energy of activation. The value of q, however, is in satisfactory agreement with the value calculated earlier, on the basis of the reaction velocity taken directly from experiment, by means of relation (7.2):  $q_0 = 3.3 \times 10^{-18}$ . Such an agreement is regarded in kinetics as a very good agreement and it was historically the first success of the theory of active collisions. Similar good results have been obtained for a number of other gas reactions—the formation of hydrogen iodide, the decomposition of nitrosyl bromide and chloride, the Butlerov reaction\* and other reactions in the gas medium and in solutions.

Now we establish the relation between the experimental (or apparent) and true energies of activation. Equation (7.12) may be represented as follows:

$$k = c T^{1/2} e^{-E/RT}$$
 or  $\ln k = \ln c + \frac{1}{2} \ln T - \frac{E}{RT}$ 

If we differentiate  $\ln k$  with respect to temperature, we get

$$\frac{d \ln k}{dT} = \frac{1}{2} \frac{1}{T} + \frac{E}{RT^2} = \frac{E + \frac{1}{2} RT}{RT^2}$$
 (7.13)

The last relation should be compared with the Arrhenius differential equation (4.12). In view of the identity of the derivatives, we find

$$E_{\Lambda} = E + \frac{1}{2} RT$$

The true energy of activation

$$E = E_{\Lambda} - \frac{1}{2} RT \tag{7.14}$$

appears to be independent of temperature if  $E_A$  is considered to be constant at a first approximation. Applying relation (7.14) to the decomposition of hydrogen iodide, HI, we obtain for the temperature 556 K:

$$E = 44,560 - \frac{1}{2} 2 \times 556 = 44,000 \text{ cal/mole}$$

<sup>\*</sup> The combined decomposition of alkyl iodide and hydrogen iodide:  $RI + HI = RH + I_2$ .

The example given shows that the difference between E and  $E_A$  is usually not great and is not infrequently found to lie within the experimental error.

If we continue to compare the basic formula of the collision theory with experiment, we pass from concentrations expressed by the number of molecules per 1 cm<sup>3</sup> to concentrations expressed by the number of moles per cubic centimeter (or per litre). Then the rate constant of a bimolecular reaction involving different molecules (7.11) may be rewritten, using the following relation

$$k_{II} \left[ \frac{\text{litre}}{\text{mole} \cdot \text{sec}} \right] = k'_{II} \frac{N_A}{1000}$$

or

$$k_{II} \left[ \frac{\text{cm}^3}{\text{mole} \cdot \text{sec}} \right] = k'_{II} N_{\Lambda}$$

where  $N_A$  is the Avogadro number. Namely,

$$k_{11} = N_{\rm A} D_{\rm AB}^2 \left\{ 8\pi RT \left( \frac{1}{M_{\rm A}} + \frac{1}{M_{\rm B}} \right) \right\}^{1/2} e^{-E/RT}$$
 (7.15)

The pre-exponential factor in formula (7.15) is designated as  $z_0$ , as before; the relation obtained in this case is outwardly reminiscent of Eq. (7.12), but the numerical values of  $z_0$  differ by the Avogadro number:

$$z_0 = N_{\rm A} D_{\rm AB}^2 \left\{ 8\pi RT \left( \frac{1}{M_{\rm A}} + \frac{1}{M_{\rm B}} \right) \right\}^{1/2} \frac{\rm cm^3}{\rm mole \cdot sec}$$
 (7.16)

Apart from the universal constants, the quantity  $z_0$  includes also the average molecular diameter  $D_{AB}$ ; for ordinary molecules the diameters do not differ strongly and are of the order of  $10^{-8}$  cm. The other variables—temperature and molecular weights—are included in  $z_0$  under the root sign. Thus, for ordinary molecules at not too high temperatures it is possible to calculate a certain averaged value of  $z_0$  and to make use of it as the reference standard in the assessment of the applicability of collision theory. \* We obtain

$$z_0 \approx 2.8 \times 10^{14} \text{ cm}^3/\text{mole} \cdot \text{sec} = 2.8 \times 10^{11} \text{ litres/mole} \cdot \text{sec}$$
 (7.17)

Reactions for which the pre-exponential factors are close to the indicated value are called **normal reactions**. From Table 7.1 which lists a number of bimolecular reactions it follows that, along with normal reactions, there are a certain number of reactions for which the experimental values of A are greater than the

<sup>\*</sup> In the case of a more exact estimation, the quantity  $T^{1/2}$  is also omitted from the expression for  $z_0$ , i.e.,  $z_0 = A_0 T^{1/2}$ . The value of  $A_0$  is of the order of  $10^{12}$ - $10^{13}$ .

	TABLE	7.1. The Co	nstants of	the Arri	nenius	Equation	
for	Selected	Bimolecular	Reactions	(Aexp in	cm <sup>3</sup> ·	mole · se	( <sup>-1</sup> )

Tempera- ture range, °C	E, kca!/mole	log A <sub>exp</sub>	P
283-508	39.0	14.1	ca. 1
283-508	44.0	13.9	ca. 0.3
250-310	33.4	14.3	ca. 1
250-310	29.8	13.7	ca. 0 <b>.</b> 2
250-310	_	14.1	ca. 1
420-480	0.0	13.7	ca. 0.2
150-250	24.5	13.0	ca. 0.04
492-570	53.2	15.5	> 1
205-241	33.9	15.2	> 1
85-250	28.2	18.8	> 1
600-1100	10.0	14.1	ca. 1
75-250	5.5	14.1	ca. 1
350-525	14.3	11.5	$10^{-3}$
25-340	10.4	11.31	$7.5 \times 10^{-4}$
25-340	8.3	11.1	$4 \times 10^{-4}$
	283-508 283-508 283-508 250-310 250-310 250-310 420-480 150-250 492-570 205-241 85-250 600-1100 75-250 350-525 25-340	283-508 39.0 283-508 44.0 250-310 33.4 250-310 29.8 250-310 — 420-480 0.0 150-250 24.5 492-570 53.2 205-241 33.9 85-250 28.2 600-1100 10.0 75-250 5.5 350-525 14.3 25-340 10.4	ture range.         kca!/mole         log Aexp           283-508         39.0         14.1           283-508         44.0         13.9           250-310         33.4         14.3           250-310         —         14.1           420-480         0.0         13.7           150-250         24.5         13.0           492-570         53.2         15.5           205-241         33.9         15.2           85-250         28.2         18.8           600-1100         10.0         14.1           75-250         5.5         14.1           350-525         14.3         11.5           25-340         10.4         11.31

calculated  $z_0$  values by 1-3 orders of magnitude. Such "fast" reactions may be accounted for by the participation in the activation process not only of two translational degrees of freedom but also of other kinds of motion, primarily, vibration. In this case the number of activating collisions should be calculated not for two quadratic terms [formula (6.39)], but for s>2 [formula (6.42)]. A more detailed treatment of this will be given at a later time in connection with unimolecular reactions (see page 189); at this point it will suffice to indicate that the values of log A equal to 15.5 and 15.2 (Table 7.1) would correspond to 4 quadratic terms. However, for ozone to be decomposed ( $\log A = 18.8$ ) there are required 18 quadratic terms. This number is thought to be too large since the vibrational motion in two molecules of ozone can provide only 12 terms and there arises the need to resort also to rotational motions. There remains the puzzle how the energy distributed over such a large number of degrees of freedom can be concentrated at the moment of collision at the bonds being ruptured. Perhaps, another explanation should be sought for.

"Slow" reactions constitute another formidable difficulty in the collision theory. As has been established, the values of pre-exponential factors of many bimolecular reactions are much lower than the "normal" value, i.e., about  $10^{14}$ . To find a way out of this difficulty, the steric or probability factor P (which is less than

unity) mentioned earlier was introduced into the expression for the rate constant, i.e., the following equation was used:

$$k_{II} = P z_0 e^{-E/RT} \tag{7.18}$$

As can be seen from Table 7.1, P attains values from 10<sup>-3</sup> to 10<sup>-4</sup>. Interesting is the attempt made by Moelwyn-Hughes to consider the applicability of the variant of collision theory under dis-

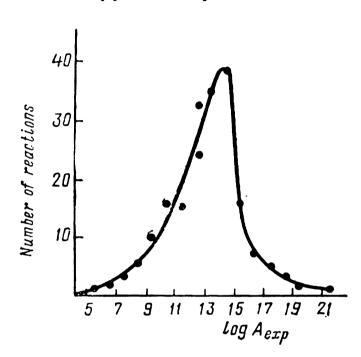


Fig. 7.3. The distribution of bimolecular reactions in solution according to the value of the pre-exponential factor (after Moelwyn-Hughes). The experimental values of A are in cm<sup>3</sup>·mole<sup>-1</sup>·sec<sup>-1</sup>.

cussion to reactions in solutions. Based on the data on 200 reactions he constructed a graph, the values of  $\log A_{(exp)}$  being plotted along the abscissa and the number of reactions along the ordinate. At  $\log A = 14.3$ , which is close to the "normal"  $\log 2.8 \times 10^{14} = 14.45$ . value. there was obtained a curve with a sharply prominent maximum (Fig. 7.3). As seen, the values of A lie between 1013 and 1014 for 35 reactions and between 1017 and 1018 for only 5 reactions. Thus, the majority of bimolecular reactions in solutions proceed with velocities. The asymmetry of the distribution curve may also be noted: the curve is steeper high rates. at This

that there are more "slow" than fast reactions. The occurrence of fast reactions may in certain cases be accounted for by the catalytic effect of the solvent. It will be expedient to return to such reactions in the discussion of homogeneous catalysis. As to slow reactions, even in this case the problem remains unsolved. To the category of especially slow reactions belong the Menshut-kin reactions which are reactions of combination of alkyl iodides with tertiary amines. For example, the formation of tetraethylammonium iodide

$$C_2H_5I + (C_2H_5)_3N \longrightarrow (C_2H_5)_4NI$$

proceeds at a rate about  $10^6$  times slower than the normal rate:  $P \approx 10^{-6}$ . In other similar cases the steric factor attains values of  $10^{-8}$  to  $10^{-9}$ . This cannot be explained by the effect of the solvent since the value of P for some gas reactions is of the same order. The present-day interpretation of P values will be taken up at a later time.

## 7.2. Unimolecular Reactions

There is ground for believing that the elementary mechanism of many reactions consists of a spontaneous decomposition of individual molecules. As we already know, such a decomposition is called monomolecular (or unimolecular). Without making any assumptions as to the mechanism of the reaction and the character of intramolecular changes we shall first show that a purely statistical treatment of the unimolecular decomposition leads to an equation for a first-order reaction, i.e., to the exponential law. The only controversial assumption, which will be adopted here, consists in the following: the decomposition of a molecule is an individual event, i.e., it is independent of the decomposition of the other molecules. Therefore, the probability P of the event that the molecule will survive and attain the lifetime t depends (under specified conditions, i.e., temperature) only on the length of this lifetime, i.e.,

$$P = f(t)$$

The probability of the molecule attaining the lifetime  $t+\tau$  will evidently be a function of  $t+\tau$ , i. e.,  $f(t+\tau)$ . On the other hand, this survival for the time  $t+\tau$  may be regarded as a complex event consisting of the survival for the time length from 0 to t and from t to  $t+\tau$ . These last events may be considered to be independent. The probability of a complex event will therefore be represented by the product of probabilities. Thus,

$$f(t+\tau) = f(t) f(\tau)$$

We differentiate this expression with respect to t, the value of  $\tau$  being assumed constant:

$$j'(t+\tau) = j'(t) f(\tau)$$

Dividing now this expression by the previous one, we get

$$\frac{f'(t+\tau)}{f(t+\tau)} = \frac{f'(t)}{f(t)}$$

Since  $\tau$  is an arbitrary quantity, then generally

$$\frac{f'(t)}{f(t)} = \text{constant}$$

On the other hand, the probability of the lifetime t=0 is apparently equal to unity, and the probability of the molecule living for an infinitely long time is equal to zero. Therefore, f(t) is a decreasing function of time and the constant with respect to the derivative of the original function is negative, i.e.,

$$\frac{\int_{1}^{r} f(t)}{\int_{1}^{r} f(t)} = -k_{I} \quad \text{or} \quad \frac{df}{\int_{1}^{r}} = -k_{I} dt$$

Hence, from the initial condition f(0) = 1 we find

$$\int = e^{-k_{\parallel}t}$$

If the probability for one molecule to survive during time t is equal to  $\exp(-k_1t)$ , then of the  $N_0$  molecules present in the system at the initial moment t=0, there will remain, on the average, by the moment t

 $N == N_0 e^{-k_{\rm I} t}$ 

This relation is in good agreement with the well-known formula (2.9) for a first-order reaction.

Thus, we arrive at the conclusion that unimolecular decompositions must be described by first-order equations. However, this is not always so, and this is apparently valid under the conditions of a statistical equilibrium when the decomposition of the molecule does not alter the concentration of molecules capable of decomposition. The statistical interpretation of the unimolecular decomposition expounded here is applicable, without reservations, to the description of spontaneous transformations of atoms of radioactive substances. It is clearly insufficient for unimolecular reactions. The rate of decomposition of molecules depends on temperature, and this is an indication that there is a relationship between reaction rate and molecular interactions.

As we continue to treat the problem statistically, we shall suppose that the molecules of substance A in an activated state with energy  $E_a$ , the equilibrium concentration of which is not affected by the course of the reaction, are subjected to unimolecular decomposition. Properly speaking, a more general assumption is made—the course of the reaction does not upset the equilibrium distribution of velocities and energies among molecules. Therefore, we may use the Boltzmann law (5.33), according to which the number of activated molecules is given by

$$N_{\mathbf{a}} = N \frac{g_{\mathbf{a}} e^{-\epsilon_{\mathbf{a}}/kT}}{\sum_{i} g_{i} e^{-\epsilon_{i}/kT}} = N \frac{g_{\mathbf{a}} e^{-\epsilon_{\mathbf{a}}/kT}}{Q}$$

Here N is the total number of molecules of substance A; g's are the statistical weights of the states; Q is the partition function. Suppose that for each of the activated molecules the probability of reacting for one second is equal to  $k_a$ . The number of molecules that will react per second is given by

$$-\frac{dN}{dt} = N \frac{\sum_{a} k_a g_a e^{-\epsilon_a/kT}}{Q} = k_1 N$$
 (7.19)

where  $k_1$  is the first-order rate constant. If we determine  $k_1$  from relation (7.19), we are to differentiate with respect to temperature, assuming  $k_a$  is constant:

$$\frac{dk_{1}}{dt} = \frac{Q \sum_{a} k_{a} \frac{\varepsilon_{a}}{kT^{2}} g_{a} e^{-\varepsilon_{a}/kT} - \sum_{a} k_{a} g_{a} e^{-\varepsilon_{a}/kT} \sum_{i} \frac{\varepsilon_{i}}{kT^{2}} g_{i} e^{-\varepsilon_{i}/kT}}{Q^{2}} = \frac{\sum_{a} k_{a} \frac{\varepsilon_{a}}{kT^{2}} g_{a} e^{-\varepsilon_{a}/kT}}{Q^{2}} - \sum_{a} k_{a} g_{a} e^{-\varepsilon_{a}/kT} \sum_{i} \frac{\varepsilon_{i}}{kT^{2}} g_{i} e^{-\varepsilon_{i}/kT}}{Q^{2}}$$

Now we divide the last expression by  $k_1$ . If we assume that the probabilities  $k_a$  are independent of the absolute value of  $\varepsilon_a$ , we shall get:

$$\frac{d \ln k_1}{dt} = \left[ \frac{\sum_{a} \varepsilon_{a} g_{a} e^{-\varepsilon_{a}/kT}}{\sum_{a} g_{a} e^{-\varepsilon_{a}/kT}} - \frac{\sum_{i} \varepsilon_{i} g_{i} e^{-\varepsilon_{i}/kT}}{\sum_{i} g_{i} e^{-\varepsilon_{i}/kT}} \right] \frac{1}{kT^{2}}$$

But the first term in square brackets is the average value of the energy of activated molecules,  $\bar{\epsilon}_a$ , and the second term is the average energy of all the molecules ( $\bar{\epsilon}_i$ ). Therefore, using also the Arrhenius equation (4.10), we get

$$\frac{d \ln k_{\rm I}}{dt} = \frac{\bar{\epsilon}_a - \bar{\epsilon}_i}{kT^2} = \frac{E_{\rm A}}{RT^2}$$

$$E_{\rm A} = N_{\rm A} \left(\bar{\epsilon}_a - \bar{\epsilon}_i\right) \frac{\text{energy}}{\text{mode}} \tag{7.20}$$

The statistical treatment of the problem leads to a consequence which is the definition of the Arrhenius energy of activation: The activation energy of a reaction is equal to the difference between the average energy of activated molecules and the average energy of all the molecules.

The problem of the origin of the energy of activation in unimolecular reactions still remains unsolved. This problem was tackled in various ways at different times; reference was even made to an external energy source in the form of incoming radiation. At present, the Lindemann hypothesis \* (1922) is universally adopted. Lindemann pointed out that the behaviour of unimolecular reactions can be explained on the basis of bimolecular collisions provided that we postulate that a time lag exists between activation and reaction during which activated molecules may

Thus.

<sup>\*</sup> Also known as the time-lag Lindemann theory. — Tr.

either react or be deactivated to ordinary molecules. To ascertain the essence of the matter, consider the reaction  $A \rightarrow B + C$  which is expected to proceed unimolecularly.

According to Lindemann, the mechanism of the reaction involves the following steps:

(1) 
$$A + A \longrightarrow A^* + A$$
  $k_1$  activation

(2) 
$$A^* \longrightarrow B + C$$
  $k_2$  decomposition

(3) 
$$A^* + A \longrightarrow A + A$$
  $k_3$  deactivation

An activated molecule appears in the first process: possibly, the relative kinetic energy of two colliding molecules is converted into the vibrational energy of the activated (energized) molecule A\*. In the second process the activated molecule is decomposed. However, as a rule, process (2) takes place not immediately after process (1) but upon the lapse of a certain finite time (which is what constitutes the main difference from a bimolecular reaction) required for the energy to be redistributed inside the molecule and to be concentrated at the bond to be broken. What has been said may be illustrated by the following example. Suppose that process (2) is the decomposition of ethane into two methyl radicals:

$$H_3C-CH_3 \longrightarrow H_3C+CH_3$$

Evidently, for such a decomposition to occur, the energy must be concentrated (vibration must be excited) at the C—C bond. But when two molecules are colliding, probably the vibrations along the peripheral C—H bonds are first excited. A certain time interval is required for the requisite amount of energy to be transferred from these bonds to the C—C bond. During this time lag the energized molecule may be deactivated by a collision with a normal molecule. In calculating the kinetics the activated molecule A\* is considered to be an unstable intermediate, to which we may apply the stationary-state (or steady-state) principle:

$$\frac{d[A^*]}{dt} = k_1[A]^2 - k_2[A^*] - k_3[A^*][A] = 0$$
 (7.21)

Hence, the concentration of activated molecules is given by

$$[A^*] = \frac{k_1 [A]^2}{k_2 + k_3 [A]}$$

The observed rate of decomposition of substance A is apparently equal to the rate of the second reaction, i.e.,

$$-\frac{d[A]}{dt} = k_2[A^*]$$

Substituting the concentration of A\* from the preceding formula

into this expression, we get an expression for the reaction rate

$$-\frac{d[A]}{dt} = \frac{k_1 k_2 [A]^2}{k_2 + k_3 [A]} = \left\{ \frac{k_1 k_2 [A]}{k_2 + k_3 [A]} \right\} [A]$$
 (7.22)

which is the result of the Lindemann hypothesis. On the whole, according to Eq. (7.22), the order of the reaction of decomposition of substance A is intermediate between the first and the second. The extreme cases should however be considered, namely:

I. The concentration (pressure) of A is high. In this case the rate of deactivation  $k_3[A^*][A]$  may appear to be much faster than the rate of decomposition  $k_2[A^*]$ , or  $k_3[A] \gg k_2$ , and the first term in the denominator of Eq. (7.22) may then be neglected as compared with the second. As a result, we get the equation for the first-order reaction:

$$-\frac{d[A]}{dt} = \frac{k_1 k_2}{k_2} [A] = k_1 [A]$$

Under these conditions there is evidently maintained the statistically equilibrium concentration of activated molecules, and the reaction takes place in accordance with the law of spontaneous decomposition (see page 179).

II. The concentration (pressure) of A is low. Then the rate of reaction (2)  $k_2$  [A\*] may appear to be much greater than the rate of deactivation  $k_3$  [A\*] [A], or

$$k_2 \gg k_3 [A]$$

Neglecting now the second term in the denominator of Eq. (7.22) we obtain a second-order equation:

$$-\frac{dA}{dt} = k_1 [A]^2$$

which results evidently in connection with the relatively long periods of time between the collisions, during which all the activated molecules, in the limit, have a chance to react. The rate of the observed reaction is now equal to the rate of the activation process (1). Thus, according to the Lindemann hypothesis [Eq. (7.22)], the rate constant calculated by the first-order law has, in general, the following form

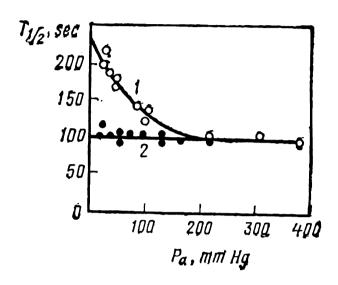
$$k_{\rm I} = \frac{k_1 k_2 [A]}{k_2 + k_3 [A]} \tag{7.23}$$

Consequently, the first-order "constant" and the time of conversion of a definite fraction of the substance must depend on the concentration or pressure of A. Figure 7.4 shows that at high pressures the half-life of diethyl ether remains constant and increases as the pressure is lowered below 200 mm Hg. The same dependence may be represented in a somewhat different form more convenient for our discussion. The quantity which is the inverse

of the constant,

$$\frac{1}{k_1} = \frac{k_3}{k_1 k_2} + \frac{1}{k_2} \frac{1}{|A|} \tag{7.24}$$

must be a linear function of the reciprocal concentration. The data provided by Fig. 7.4 are represented by a straight line in



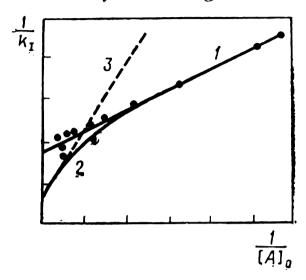


Fig. 7.4. The half-life of diethyl ether against the initial pressure  $(P_0)$  of the ether:

1 - without hydrogen; 2 - with hydrogen added.

Fig. 7.5. The rate constant of a unimolecular reaction in the coordinates  $1/K_1$  and  $1/[A_0]$ :

1—diethyl ether; 2—ordinary departure from the straight-line dependence; 3—straight line corresponding to Eq. (7.23).

Fig. 7.5. As can be seen, the points are spread in the vicinity of the coordinate origin, but still we can plot a straight line. In most of the reactions investigated in this way, say in the decomposition of azomethane \*,

$$CH_3NNCH_3 \longrightarrow C_2H_6 + N_2$$

no straight line is obtained. Figure 7.5 shows the approximate course of the experimental curve (curve 2). On the whole, we should speak of a qualitative confirmation of the theory: with increasing pressure the first-order rate constant tends to a constant value  $(k_{\infty})$ . To put it in a different way: for every reaction there exists a minimum initial pressure, below which the first-order rate constant decreases. Table 7.2 lists some data for a number of unimolecular reactions, including minimum initial pressures. It can be seen that the minimum initial pressure appears to be the lowest for the decomposition of nitrogen pentoxide (0.006 mm); its determination presented considerable difficulties. It should be emphasized that we are speaking here of the effect of the *initial* pressure on  $k_1$  since within separate experiments, i.e., at given  $P_0$ , the first-order rate constant remains constant,

<sup>\*</sup> We shall return to this reaction at a later time in connection with the Kassel theory.

				iccuiui
<b>D</b>	Minimum Initial pressure,	Constants in Arri	nenius equation ‱	Temperature,
Reacting substance	P <sub>0</sub> (min), mm Hg	A <sub>exp</sub> , sec-1	E <sub>A</sub> , kcal/mole	K
N <sub>2</sub> O <sub>5</sub>	0.06	4.5×10 <sup>13</sup>	24.5	273-338
CH <sub>3</sub> NNCH <sub>3</sub>	40	$1.1 \times 10^{16}$	50.0	551-603
CH <sub>3</sub> NNC <sub>3</sub> H <sub>7</sub>	25	$2.8\times10^{15}$	46.0	523-605
$C_2H_5OC_2H_5$	150	$3.1 \times 10^{11}$	51.8	700-860
C <sub>2</sub> H <sub>5</sub> Cl	8	$3.9\times10^{14}$	60.8	720-770
CH <sub>3</sub> CHCl <sub>2</sub>	20	$4.5\times10^{11}$	48.3	685-722
CH₃CHCICH₃	4	$2.5\times10^{13}$	50.5	673-683
CH <sub>3</sub> CCl <sub>2</sub> CH <sub>3</sub>	10	$7.9\times10^{11}$	43.9	603-690
C <sub>2</sub> H <sub>5</sub> NH <sub>2</sub> CH <sub>2</sub> \	50	$2.9 \times 10^{9}$	42.5	773-813
CH <sub>2</sub> O	285	$8.4 \times 10^{12}$	50.9	651-788

TABLE 7.2. Selected Reactions Considered to be Unimolecular

even if the pressure of the starting substance becomes less than the "minimum" pressure during the course of the experiment. Here arises the question as to the role of reaction products and added foreign inert gases. Thus, in the decomposition of diethyl ether the addition of hydrogen to the starting ether prevents the decrease of the constant, maintaining it at the level of  $k_{\infty}$ . Figure 7.4 demonstrates the effect of hydrogen (curve 2). These phenomena may all be accounted for by the participation of the reaction products and of the added hydrogen in the activation process

TABLE 7.3. The Half-Lives of Isopropyl Aldehyde in the Absence and Presence of Hydrogen

Initial pressure of aldehyde, mm Hg	Initial pressure of hydrogen, mm Hg	Half-life period T <sub>1/2</sub> , sec	Initial pressure of aldehyde, mm Hg	Initial pressure of hydrogen, mm Hg	Half-life period T <sub>1/2</sub> , sec
271 130 40	0 0 0	552 645 866	287 40 46 45	407 211 402 610	600 622 552 585

I of the Lindemann mechanism (Table 7.3). A similar compensating property is also exhibited by other substances. As seen from Table 7.3, at a high pressure of the aldehyde, the hydrogen added

has no substantial effect on the course of the reaction, but at a low pressure it reduces the half-life period to the normal value equal approximately to 600 sec. Not only hydrogen can play the role of such a peculiar "catalyst" or, more exactly, an energy-transfer agent.

The first order during the course of this experiment is maintained even in the decomposition of methylisopropyl ether:

$$CH_3-O-C_3H_7 \longrightarrow CH_4+CO+C_2H_6$$

Here there is no hydrogen in the products and its role is played by ethane, as has been shown by special experiments.

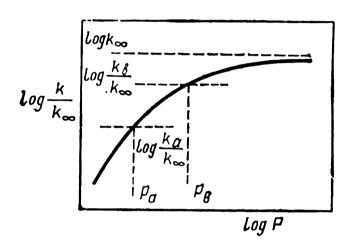


Fig. 7.6. Determination of the effectiveness of various gases in maintaining the rate of a unimolecular reaction.

The study of the ability of any gas to maintain the rate of a unimolecular reaction is employed as a method of determining the rate of energy transfer from some molecules to other molecules. At pressure P the rate constant of the decomposition of substance A is equal to  $k_a$ . Figure 7.6 gives the preliminarily determined dependence of the relative values of the rate constants  $(k/k_{\infty})$  for the decomposition of substance A on pressure. When a chemically inert gas B, whose pressure is P, is

added, the rate constant of the decomposition of A increases from  $k_a$  to  $k_b$ . Then, as compared with A the relative efficiency of substance B in transferring energy to substance A will be expressed by the relation  $(P_b - P_a)/P$ . Having chosen the kinetic collision diameters, we can then estimate the relative efficiency of collisions (Table 7.4). On the basis of the data presented in Table 7.4 it may be concluded that the efficiency of the energy transfer is the higher, the more complex is the molecule, but the efficiency limit is soon reached after a while, beyond which it does not increase with increasing complexity of the molecule. Therefore, the assumption of the theory of unimolecular reactions regarding the exchange of energy during each collision between molecules of not too simple a structure is possibly correct. Since a vibrationally excited, i.e, activated, diatomic molecule exists, on an average, for about 10-13 sec in accordance with the vibration period, and the time between collisions at P=1 atm is about  $10^{-10}$  [Eq. (6.23)], the "unimolecular" decomposition of diatomic molecules can be observed only in the second-order region. In other words, it occurs immediately

TABLE 7.4. The Relative Efficiency of Various Gases in Energy Transfer on Collisions

	<i>ر.</i> ث	492	448	310	50.5	-37	250	653	
	CO <sub>2</sub>	1	ı	0.25	0.39	0.45	ŧ	1.3	
	H <sub>2</sub> O	0.74	0.44	0.46	ı	1	1	1.5	
	ON	ı	i	1	0.30	1	1	1	
	00	0.08	I	0.13	1	1	ı	1	
Relative efficiency on addition of	F <sub>2</sub>	1	1	1	i	0.33	1.13	Ī	
y on ad	Ô	1	1	1	1	1.2	1.13	0.23	
efficienc	ž	0.07	0.21	0.21	0.23	0.21	1.01	0.24	
Relative	Ë	0.12	0.10	I	١	l	l	1	
	Xe	1	1	1	0.19	1	1	1	
	Kr	l	l		0.21	1	1	0.18	
	Ar	0.07	0.21	1	0.15	0.40	0.82	0.20	
	Ne	1	0.12	1	0.09	1	1	0.47	
	He	0.05	0.07	0.07	0.07	0.07	0.40	99.0	
Start-	sub. stance	-	_	-	_		_	_	
Compound subjected	to unimolecular decomposition	Cyclopropane	Cyclobutane	Azomethane	Nitrogen pentoxide	Fluorine dioxide	Fluorine oxide	Nitrogen oxide	

after a bimolecular activating collision, i.e., it is by itself bimolecular.

Thus, from the standpoint of the theory under consideration, there is no fundamental difference between bimolecular and unimolecular processes: they are two limiting consequences of the bimolecular act of activation.

In spite of the fact that the Lindemann hypothesis is in accord with certain experimental data (though the agreement is rather qualitative), it has proved, on the whole, unsatisfactory. Thus, it may be assumed that in unimolecular reactions the activation occurs bimolecularly on collision of two molecules with a relative kinetic energy along the line of the centres equal to or greater than E (see page 173). Then, evidently, the highest theoretically possible reaction rate (assuming the absence of deactivating collisions) must be equal to the number of activating collisions, i.e.,

$$-\left(\frac{dn}{dt}\right)_{\text{largest}} = 2D^2 \left\{\frac{\pi RT}{M}\right\}^{1/2} e^{-E/RT} n^2 \tag{7.25}$$

According to the basic law of kinetics, the rate is expressed by a first-order equation:

$$-\frac{dn}{dt} = k_{\rm I} n \tag{7.26}$$

By comparing Eqs. (7.25) and (7.26) we find an expression for the largest rate constant on such an assumption:

 $(k_I)_{largest} = 2D^2 \left\{ \frac{\pi RT}{M} \right\}^{1/2} n e^{-E/RT}$  where  $(Z_0)_{largest} = 2D^2 \left\{ \frac{\pi RT}{M} \right\}^{1/2} n$  (sec-1) is the collision frequency for one molecule. The thus introduced quantity  $(Z_0)_{largest}$  is however found to be by many orders of magnitude smaller than the experimental value. Indeed, let us consider the decomposition of acetone at 800 K:

$$CH_3COCH_3 \longrightarrow CO + C_2H_4 + H_2$$

The kinetic diameter of the acetone molecule  $D \approx 5 \times 10^{-8}$  cm; let its concentration be equal to 1 mole/22.4 litres. We get

$$(Z_0)_{\text{largest}} = 2 (5 \times 10^{-8})^2 \left\{ \frac{3.14 \times 8.3 \times 10^7 \times 800}{58} \right\}^{1/2} \times \frac{6.02 \times 10^{23}}{22.400} = 8.1 \times 10^9 \text{ sec}^{-1}$$

The experimental value of  $Z_0 \approx A$  may be taken from the Arrhenius empirical equation:

$$(k_1)_{\text{exp}} = 1.5 \times 10^{15} \times e^{-E/RT}$$

In other words, it turns out that the experimental value of  $Z_0$  is  $1.5 \times 10^{15}/8.1 \times 10^9 \approx 2 \times 10^5$  times greater than the "largest"

theoretical value. Thus, even if we assume that each collision of sufficient energy is activating and all the activated molecules have a chance to react, the resulting value of  $Z_0$  is by 5 orders of magnitude lower than the experimental value. The theory thus formulated is apparently not suitable and needs to be corrected.

The path suggested by Hinshelwood for perfecting the collision theory of unimolecular reactions consists in the following. Unimolecular decomposition is experienced by relatively complex molecules, the activation of which may involve not only two translational degrees of freedom but also any number of other kinds of motion, primarily vibration, and in some cases rotation as well. If the molecule consists of m atoms, then the total number of vibrational degrees of freedom can be found from the following relation:

$$F_{\text{vib}} = 3m - x$$

where x = 5 for a linear molecule, 6 for a nonlinear molecule, and 7 if there is one degree of freedom of internal rotation. As an

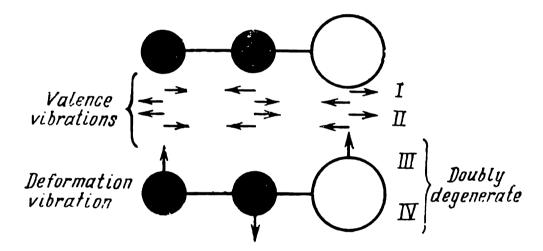


Fig. 7.7. Vibrations in a stable linear triatomic molecule.

example, let us consider a linear triatomic molecule, say,  $N_2O$  (Fig. 7.7). It is subject to four modes of vibration—two valence and two deformation vibrations, and more exactly, one doubly-degenerate deformation, which can occur in two mutually perpendicular planes.

Suppose that f vibrational degrees of freedom (evidently,  $f \leq F_{\text{vib}}$ ) participate in the activation process. Then, since the energy of each mode of vibration (harmonic) is expressed by two quadratic terms [Eq. (6.38)], all the energy involved in the activation process will be expressed by s quadratic terms:

$$s = 2f + 2$$

Now the number of active (activating) collisions will be determined not by formula (6.39) but by a more complicated relation, (6.40). We make use of a simplified variant of this relation, which

is applicable on condition that  $E \gg RT$ , i.e., Eq. (6.42):

$$Z_E = Z \frac{\left(\frac{E}{RT}\right)^{\frac{1}{2}s-1}}{\left(\frac{1}{2}s-1\right)!} e^{-E/RT}$$

The point is that the ratio  $Z_E/Z$  increases rapidly with increasing s. For example, at 300 K and E=21,000 cal/mole we have the following values for the ratio  $Z_E/Z$ :

s 
$$\frac{Z_E}{Z}$$
2  $6.3 \times 10^{-16}$ 
4  $3864 \times 10^{-16}$ 
8  $16,100,000 \times 10^{-16}$ 

In other words, when we pass over from two quadratic terms, in which case formula (6.39) is valid, to eight terms, the number of activating collisions increases almost by  $3 \times 10^6$  times.

The rate constant of a unimolecular reaction should be written, according to Hinshelwood, as follows:

$$k_{I} = \left[ Z_{0} \frac{\left(\frac{E}{RT}\right)^{\frac{1}{2}s - 1}}{\left(\frac{1}{2}s - 1\right)!} \right] e^{-E/RT}$$
 (7.27)

To the experimental exponential factor of the Arrhenius equation there will now correspond the quantity in square brackets. As has been shown by calculations, the theory can be brought into agreement with experiment by selecting the appropriate values of s (Table 7.5).

TABLE 7.5. The Number of Quadratic Terms Satisfying the Observed Rate of the Decomposition Reaction

Compound being decomposed	s	$s^{-2}$	f	Compound being decomposed	s	's-2	+
C <sub>2</sub> H <sub>5</sub> Cl	12	10	5	C <sub>2</sub> H <sub>5</sub> OC <sub>2</sub> H <sub>5</sub>	8	6	3
CH <sub>3</sub> OCH <sub>3</sub>	11	9	4-5	CH <sub>3</sub> NNCH <sub>3</sub>	25	23	11-1 <b>2</b>

The number of vibrational degrees of freedom, f, required to ensure the observed rates, is less than 3m-6 and therefore it may be considered to be plausible. And that is all! The theory cannot predict the number f and explain why in the decomposition of diethyl alcohol it suffices to assume f=3 and in the case of azomethane the number f amounts to 11-12.

## 7.3. Other Theories of Unimolecular Reactions

The Kassel Theory. The theory developed by Kassel is concerned with a molecular model which is a set of weakly coupled harmonic oscillators. Therefore, they have no substantial effect on one another, but nevertheless the energy can be transferred from one oscillator to another, i.e., can be spontaneously redistributed inside the molecule. The condition for the occurrence of reaction is the localization of a sufficient amount of energy in one of the oscillators.

In this connection let us consider a group of s oscillators having the same frequency v. To apply the Boltzmann distribution law in the form

$$N_{i} = N \frac{g_{j}e^{-\epsilon_{j}/kT}}{\sum_{i} g_{i}e^{-\epsilon_{i}/kT}} = N \frac{g_{j}e^{-\epsilon_{j}/kT}}{Q}$$
 (7.28)

we determine the quantum contribution or the degeneracy of the system. For a system of oscillators with a specified number of quanta  $g_j$  is expressed by a number of various methods, by means of which the j quanta can be distributed over s oscillators. To solve this problem, it is most convenient to write a series consisting of j crosses and s+1 lines:

Thus, the crosses will prove to be distributed among s groups. Further, while seeking to find the number of distributions, we shall transpose the crosses and lines, taking into account that the extreme lines are not subject to transposition since they delineate the boundaries of the system. Therefore the number of the lines to be transposed will be s-1, and the total number of the elements being transposed will be j+s-1. If all the elements were distinguishable, the number of transpositions would then be equal to (s+j-1)! But, as a matter of fact, the j and s-1 elements are identical. Hence, the number of distinguishable configurations is equal to

$$g_j = \frac{(j+s-1)!}{j! (s-1)!} \tag{7.29}$$

The partition function may now be written thus:

$$Q = \sum_{i=0}^{i=\infty} \frac{(i+s-1)!}{i! (s-1)!} e^{-ih\nu/kT} = 1 + \frac{s}{1} e^{-h\nu/kT} + \frac{s (s+1)}{1 \times 2} e^{-2h\nu/kT} + \dots = (1 - e^{-h\nu/kT})^{-s}$$

$$(7.30)$$

and the distribution law (7.28) may be represented in the following form:

$$\frac{N_j}{N} = \frac{(j+s-1)!}{j! (s-1)!} \left(1 - e^{-h\nu/kT}\right)^s e^{-jh\nu/kT} \tag{7.31}$$

Then we can find the probability of the event that if s oscillators have j quanta, at least m quanta will be concentrated in one of them. The oscillator with m quanta under consideration may be likened, say, to the first group of crosses from the left. Let this group contain m crosses. Therefore, in calculating the number of transpositions these crosses are not taken into account. The quantum weight of all the states in which s oscillators have j quanta and one oscillator has at least m quanta, will be

$$\frac{(j-m+s-1)!}{(j-m)!(s-1)!} \tag{7.32}$$

The probability of such a distribution of quanta (and of energy) is found by dividing Eq. (7.32) by the total quantum weight (7.29). It equals

$$\frac{(j-m+s-1)!\ j!}{(j-m)!\ (j+s-1)!} \tag{7.33}$$

Calculation of the reaction rate at high pressures. In this case we may assume the equilibrium concentrations of molecules capable of reacting and write the rate constant in the form of the earlier used relation of the type (7.19):

$$k = -\frac{1}{N} \cdot \frac{dN}{dt} = \frac{\sum_{j} k_{j} g_{j} e^{-\epsilon_{j}/kT}}{\sum_{i} g_{i} e^{-\epsilon_{i}/kT}}$$
(7.34)

in which the summation is carried out over the reactive states j with partial rate constants  $k_j$  in the numerator and over all the numerator and over all the states in the denominator.

Then, we make use, as before, of the simplest model of the molecule with s weakly coupled harmonic oscillators, so that the energy can be spontaneously transferred from one oscillator to another. The oscillators are quantized and all have the same frequency v. The number of molecules in the state j is given by the familiar formula (7.31):

$$N_{j} = N \frac{(j+s-1)!}{j! (s-1)!} (1 - e^{-h\nu/kT})^{s} e^{-jh\nu/kT}$$

The next step in the calculations is the determination of the partial values of the rate constant  $k_l$ . It is most convenient to assume

that  $k_j = 0$  at j < m and  $k_j = \lambda = \text{const}$  at  $j \ge m$ , the product mhv representing the energy required for the reaction (for example, the bond-breaking energy). Then the limiting value of the rate constant of a unimolecular reaction will be given by the following relation

$$k_{\infty} = \lambda \left( 1 - e^{-h\nu/kT} \right)^{s} \sum_{j=m}^{\infty} \frac{(j+s-1)!}{j! (s-1)!} e^{-jh\nu/kT}$$
 (7.35)

According to Kassel, this formula cannot be simplified. The series presented by the formula can be calculated but the author himself rejects the formula, considering the form of the dependence of  $k_i$  on the number of quanta on the critical oscillator to be too simple. Further, Kassel assumes the migration of energy inside the molecule at a constant velocity and considers  $k_i$  to be proportional to the fraction of molecules out of the total number of molecules having j quanta, in which there are at least m quanta per a certain chosen oscillator. Use is made of formula (7.33) and  $k_i$  is taken to be proportional to the probability expressed by this formula:

$$k_j = A \frac{j! (j - m + s - 1)!}{(j - m)! (j + s - 1)!}$$
(7.36)

If j is large, then the expression for the probability can be simplified, in which case the partial constant assumes the following form

$$k_{j} = A \left( \frac{j - m}{j} \right)^{s - 1}$$

The total number of quanta j is proportional to the total vibrational energy of the molecule,  $\epsilon$ , and m is proportional to the energy  $\epsilon_0$ , which is the minimum energy required for the reaction. Therefore

$$k_{f} = \Lambda \left(\frac{\varepsilon - \varepsilon_{0}}{\varepsilon}\right)^{s-1} \tag{7.37}$$

Thus, the active molecules are not all equally reactive:  $k_i$  depends on the excess of energy in the molecule over the minimum amount of energy,  $\epsilon_0$ , needed for the reaction. To determine the overall rate constant  $k_i$ , a summation or integration must be carried out over all the possible values of energy from  $\epsilon_0$  to infinity. The graphical integration carried out has demonstrated that it is possible to bring the theory into agreement with experiment on the assumption of a plausible number of oscillators.

Another method of determining the overall rate constant is also used, in which  $k_i$  from Eq. (7.36) is substituted into the

expression for  $k_{\infty}$  (7.35). Now, instead of Eq. (7.35) we get

$$k_{\infty} = A(1 - e^{-h\nu/kT})^{s} \sum_{j=m}^{\infty} \frac{(j+s-1)! \ j! \ (j-m+s-1)!}{j! \ (s-1)! \ (j-m)! \ (j+s-1)!} e^{-jh\nu/kT} =$$

$$= A(1 - e^{-h\nu/kT})^{s} \sum_{j=m}^{\infty} \frac{(j-m+s-1)!}{(s-1)! \ (j-m)!} e^{-jh\nu/kT} =$$

$$= Ae^{-mh\nu/kT} \left(1 - e^{-h\nu/kT}\right)^{s} \sum_{p=0}^{\infty} \frac{(p+s-1)!}{p! \ (s-1)!} e^{-ph\nu/kT}$$

In the last relation the substitution p = j - m is made. But, as can easily be seen \*,

$$(1 - e^{-h\nu/kT})^{-s} = \sum_{p}^{\infty} \frac{(p+s-1)!}{p! (s-1)!} e^{-ph\nu/kT}$$

Therefore, the expression for the limiting rate constant is considerably simplified:

$$k_{\infty} = Ae^{-mhv'kT} \tag{7.38}$$

Here  $mh_V = \epsilon_0$  is called the critical energy. Such is in general the term used for the minimum energy which a molecule must possess in order to react. According to this theory, the energy of activation is equal to the critical energy only at high pressures.

Calculation of the reaction rate at any pressure. Since the Boltzmann law describes the energy distribution in an equilibrium molecular system, its application to a reacting gas is strictly speaking illegitimate and does not lead to appreciable errors only at sufficiently high pressures. The balance of active molecules is determined, according to the Lindemann hypothesis, by the competition of three processes: the formation of activated molecules by collision, their deactivation and disappearance as the result of the reaction.

In order to calculate the concentration of active molecules, it is assumed that on each collision the energy is redistributed, as a result of which there appear two inactive molecules. Thus, the rate of deactivation by collisions is approximately equal to the frequency of collisions between such molecules. If we provisionally assume the absence of a reaction, then, extending the principle of microscopic reversibility to gases, we have to admit that nearly all active molecules are created by means of binary collisions between normal molecules. Using the kinetic theory of gas-

<sup>\*</sup> Compare with relation (7.30).

es, we find the rate of formation of active molecules with j quanta:

$$aNN_{i}$$

where a is the collision frequency at  $N=N_j=1$ , i.e., Eq. (6.28),  $a=2D^2(\pi kT/m)^{1/2}$ , and  $N_j$  is the equilibrium number of molecules possessing j quanta, which is determined by relation (7.31). The rate of deactivation of these molecules on collision is equal to  $aNZ_j$ , where  $Z_j$  is the actual number of such molecules in 1 cm<sup>3</sup>. The rate of reaction of activated molecules equals  $k_jZ_j$ . In the stationary state

$$aNN_i = aNZ_i + k_iZ_i$$

Hence

$$Z_{j} = \frac{N_{j}}{1 + \frac{k_{j}}{aN}}$$

and the rate constant of the reaction

$$k = \frac{1}{N} \sum_{j=m}^{\infty} k_j Z_j \tag{7.39}$$

If, as before, we first make the simplest assumption that

$$k_j = 0$$
 at  $j < m$  and  $k_j = \lambda$  at  $j \equiv m$ 

then, substituting these values into Eq. (7.39) and comparing the result with Eq. (7.31) and (7.35), we shall find that

$$k = \frac{\lambda}{1 + \frac{\lambda}{aN}} \sum_{j=m}^{\infty} \frac{N_j}{N} = \frac{k_{\infty}}{1 + \frac{\lambda}{aN}}$$
 (7.40)

or

$$\frac{k_{\infty}}{k} = 1 + \frac{\lambda}{aN} \tag{7.41}$$

Thus, with the assumptions made concerning  $k_j$  the dependence of 1/k on 1/N (or on 1/P) will be linear with a coefficient being proportional to  $1/T^{1/2}$ . This is in harmony with the requirement of the Lindemann-Hinshelwood theory, but does not agree in general with experimental data.

But if we make another assumption and adopt the definition given by relation (7.36) for the partial constant  $k_i$ , we can, in the long run, obtain the following relation for the ratio of the constant at a given pressure to the limiting constant:

$$\frac{k}{k_{\infty}} = \left(1 - e^{-h\nu/kT}\right)^{s} \sum_{p=0}^{\infty} \frac{\frac{(p+s-1)!}{p! (s-1)!} e^{-ph\nu/kT}}{1 + \frac{A}{aN} \cdot \frac{(p+m)! (p+s-1)!}{p! (p+m+s-1)!}}$$
(7.42)

This relationship can be shown by simple reasoning to give a decrease of the ratio  $k/k_{\infty}$  with rise of temperature.

As an example of the application of the Kassel theory, let us consider, once again in more detail, the decomposition of azomethane studied by Ramsperger. The main reaction proceeds apparently according to the equation

$$CH_3NNCH_3 \longrightarrow C_2H_6 + N_2$$

This reaction is accompanied by a weak side reaction since the products contain about 1.7 per cent of unsaturated hydrocarbons.

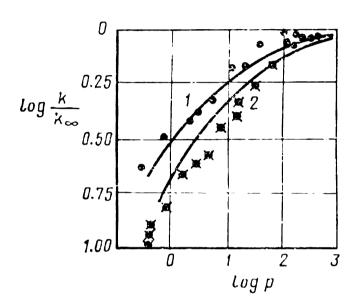


Fig. 7.8. The rate constant of the decomposition of azomethane versus its initial pressure:

The points are the experimental data; the solid lines are the theoretical curves according to Kassel (I-20) °C and 2-330 °C).

The reaction was studied at pressures ranging from 25 to 760 mm Hg and temperatures from 280 to 330 °C. Under these conditions the reaction is homogeneous and is well described at high pressures by a first-order equation. At low pressures reaction in experiments taken separately also obeys the first-order law, but the constants decrease as the initial pressure is lowered. The fact that each separate experiment yields satisfactory first-order constants is an indication of the efficiency of activating sions between azomethane and the reaction products. thus maintain the reaction rate

at the initial level. According to Ramsperger, the principal role is played here by ethane and the nitrogen is less effective. The results of these investigations are presented in Table 7.6 and in Fig. 7.8. According to these data, the average limiting rate constants are equal to  $13.8 \times 10^{-5}$  sec<sup>-1</sup> at 290 °C and to 309  $\times$   $\times 10^{-5}$  sec<sup>-1</sup> at 330 °C. Hence, we can obtain the Arrhenius equation with the following values of the constants:

$$k = 3.13 \times 10^{16} e^{-5.2.440^{7} RT} \text{ sec}^{-1}$$

As has been found, the dependence of k on pressure can be satisfactorily described by means of the Kassel theory if we adopt, for this particular case, a molecular model containing 18 vibrational degrees of freedom with such a frequency that 25  $N_A h \nu = 52,440$  cal/mole. The gas-kinetic diameter should be put equal to  $3.98 \times 10^{-8}$  cm. The calculated values of  $k/k_{\infty}$  at several pressures and two temperatures are given in Table 7.7. Figure 7.8 pre-

TABLE 7.6. The Rate Constants for Decomposition of Azomethane at Temperatures 290 and 330 °C and Various Initial Pressures (after Ramsperger)

Piessure, nen Hg	$k \cdot 10^5$ , sec <sup>-1</sup>	Pressure mm Hg	R·10 <sup>5</sup> , sec <sup>-1</sup>	Pressure, mm Hg	$k \cdot 10^5, \text{ sec}^{-1}$
		t =	290 °C		
70 <b>7.9</b>	13.5	44.07	11.8	2.587	5.8
3 <b>75.0</b>	13.7	23.51	9.7	1.989	5.3
320.0	13.7	12.03	9.0	0.879	4.5
191.0	13.2	5.818	6.9	309	3.2
		t = 3	330 °C		·
486.8	296	33.28	176	1.510	69
392.6	282	16.21	145	1.267	60
269.6	276	14.39	131	0.873	48
235.3	282	7.507	110	0.505	40
200.0	269	4.531	84	0.380	36
143.6	265	2.870	75	0.259	31
56.46	213	2.648	79		_

sents the results of theoretical calculations in the form of solid curves; as can be seen, these results in general describe reasonably well the course of the experimental dependence of  $k/k_{\infty}$  on pressure. Note also that the values of  $k/k_{\infty}$  are higher at a low temperature—this is one of the important consequences of the theory. The distances between the theoretical curves are however smaller than those between the experimental curves. A better agreement of curve 2 (Fig. 7.8) (330 °C) could be obtained by using somewhat different values of the constants, say, of the diameter D. This would however look like adjusting theory to experiment for the given concrete conditions.

Calculations similar to those given here have been performed by Kassel for a number of other azo compounds, and also for aliphatic ethers. \* On the whole, there have been obtained results which describe satisfactorily the experimental data. In the following series of azo compounds: azomethane, azoisopropane, and methylisopropyl diimide, there is observed a distinct regularity: the numbers of vibrational degrees of freedom in these com-

<sup>\*</sup> Kassel, L. S., The Kinetics of Homogeneous Gas Reactions. Chemical Catalog Company, New York, 1932.

Pressure, mm Hg	$k/k_{\infty}$	Pressure, mm Hg	$k/k_{\infty}$
$t = 330^{\circ}$	PC	t = 200	°C
5870	0.983	530	0.938
587	0.909	53	0.773
58.7	0.707	5.3	0.490
5.87	0.414	0.53	0.223
0.587	0.173	0.053	0.0708
0.0587	0.0512		

TABLE 7.7. The Calculated Values of  $k/k_{\infty}$  for the Decomposition of Azomethane at s = 18, m = 25,  $D = 3.98 \times 10^{-8}$  cm

pounds are equal to 24, 42, and 60, and the numbers of classical quadratic terms required to bring theory into harmony with experiment are, respectively, 25, 33 and > 40, being nearly equal to half of the total number of possible terms.

For ethers, no such regularity has been observed, and the number of quadratic terms, required for the description of their decomposition reactions, does not increase with increasing number of atoms in the molecule. Such a decomposition in the behaviour of ethers and azo compounds is difficult to understand without making additional, more or less groundless, assumptions.

And still the Kassel theory and the similar Rice-Ramsperger theory \* were nevertheless at their time a considerable step forward as compared with the simple Lindemann-Hinshelwood theory. This latter theory, as must be clear from the previous discussion, assumes identical partial rate constants for all types of activated molecules provided that their energy is greater than the critical energy and, on the whole, fails to describe satisfactorily the experimentally observed regularities.

The Slater Theory. The theory developed by Slater is one of the most developed theories of unimolecular reactions. We shall give only a general survey of the Slater theory (for a detailed treatment of this theory, the reader is referred to the articles and the monograph written by Slater \*\*). The Slater theory pictures

<sup>\*</sup> The combined Rice, Ramsperger and Kassel treatment is known as the

RRK theory. — Tr.

\*\* Slater, N. B., Phil. Trans. Roy. Soc. London, 246A, 57 (1953); Proc. Roy.
Soc. London, 218A, 224 (1953); Proc. Leeds Phil. Soc., 6, 268 (1955). Slater, N. B.,
Theory of Unimolecular Reactions, Cornell Univ. Press, Ithaca, New York, 1959.

a polyatomic molecule as an assembly of harmonic oscillators. The motion of atoms in a molecule is described by the variation of a series of internal coordinates  $q_1, q_2, q_3 \ldots$ . When the corresponding coordinate attains a critical value  $q_0$ , there takes place a chemical conversion. Coordinates can be chosen by any most convenient method. Thus, for the breakdown of a molecule into two radicals the distance along the bond being broken between two atoms must attain the critical value. For a *cis-trans* isomerization the coordinate that reaches the critical value will be the distance between the nuclei of two non-bonded atoms. If use is made of angular coordinates, the reaction must occur when the appropriate angle reaches the critical value.

Since all the oscillators are harmonic, their potential energies are expressed by quadratic functions of the coordinates  $q_i$ . The internal motion can be resolved into a series of vibrational motions 1, 2, 3, ..., with frequencies  $v_1, v_2, v_3, \ldots$ , energies  $\varepsilon_1, \varepsilon_2, \varepsilon_3, \ldots$ , and phases  $\psi_1, \psi_2, \psi_3, \ldots$ . The vibration frequencies are assumed to be independent. As a consequence, in a molecule that does not interact with other molecules, the energies and phases of these motions are independent and constant. They are changed only by collisions.

At this point the theory under consideration differs from the majority of other theories, say, the Kassel theory, which assumes the presence of a linkage between the oscillators and the transfer of energy from one oscillator to another. After a collision the change of a certain coordinate q is a function only of time and may be specified in the form

$$q_i = \sum_{s=1}^n a_s \cos 2\pi \left( v_s t + \psi_s \right); \quad a_s = a_s \sqrt{\varepsilon_s}; \quad a_s \neq 0$$
 (7.43)

The proportionality factors  $\alpha_s$  are characteristic constants for each coordinate q. They can in principle be obtained from the force and inertial constants of the molecules. The number n is in most cases the total number of modes of vibration of the molecule and has the highest value 3m-6 for a non-linear molecule and 3m-5 for a linear molecule. The number n may however be less than the highest value, if, for example, some of the changes of q are insignificant (the corresponding  $\alpha$ 's are small) and their contribution may be ignored. A molecule cannot react unless the following condition is satisfied:

$$\sum |a_s| \equiv \sum |\alpha_s| \sqrt{\varepsilon_s} \equiv q_0 \tag{7.44}$$

The point is that, as can be shown, unless this condition is satisfied, q cannot attain the critical value  $q_0$ . The value of  $\varepsilon_s$  that satisfies this requirement and corresponds at the same time to the

minimum total energy are found to be equal to

$$\varepsilon_s = q_0^2 \alpha_s^2 \alpha^{-4}$$

where  $\alpha^2 = \sum \alpha_s^2$ . Hence, the lowest or critical energy of the molecule,  $\epsilon_0$ , required for the reaction to occur is given by the relation

$$\varepsilon_0 = \frac{E_0}{N_{\Lambda}} = \frac{q_0^2}{\alpha^2}$$

in which  $N_A$  is the Avogadro number. Any molecule containing the suitably distributed energy  $\varepsilon_0$  and left to itself will react.

Having established the requisite minimum conditions for the occurrence of a reaction, we are now in a position to calculate its rate. To do this, we must first find the *fraction* of molecules in the system, that satisfy the necessary energy requirements. Second, we must establish the velocity with which the molecules possessing various energies will react. The overall reaction rate will then be expressed by the sum of the products of the type  $C_{\varepsilon}r_{\varepsilon}$ , where  $C_{\varepsilon}$  is the concentration of molecules with an energy content within the given interval, and  $r_{\varepsilon}$  is the average rate of their conversion.

The number of molecules (or their fraction) possessing energy in the given interval can be found, assuming that the state of the system does not differ significantly from the equilibrium state. Then the number of molecules out of the total number C, whose energies lie within the limits  $(\varepsilon_1, \varepsilon_1 + d\varepsilon_1) \dots (\varepsilon_n, \varepsilon_n + d\varepsilon_n)$  will be given by the following relation

$$Cf(\varepsilon) d\varepsilon_1 \dots d\varepsilon_n; \quad f(\varepsilon) \equiv \frac{e^{-\sum \varepsilon_S/kT}}{(kT)^n}$$
 (7.45)

The fraction of molecules reacting per second, out of the total number of molecules containing energy in the form of the components  $\varepsilon_1, \varepsilon_2, \varepsilon_3, \ldots, \varepsilon_n$  will be equal to L which is the average rate of attainment of the critical value of q  $(q_0)$ . This proposition is important in the theory since it is exactly this proposition that introduces the time factor into the treatment.

Now we can write the overall rate constant for a unimolecular reaction

$$k \equiv -\frac{1}{C} \cdot \frac{dC}{dt} = \int \dots \int L[(\epsilon) d\epsilon_1 \dots d\epsilon_n]$$
 (7.46)

In this expression the integral is taken over the energy values for which  $\varepsilon_s$  is greater than zero, which satisfy Eq. (7.44). Into the expression for the rate constant (7.46) there must be inserted

the value of L from the formula

$$L = \frac{1}{4\pi^2} \int_{-\infty}^{+\infty} \frac{\cos(q_0 x)}{y^2} \left\{ \prod_{s=1}^{n} J_0(a_s x) - \prod_{s=1}^{n} J_0(a_s \sqrt{x^2 + 4\pi^2 y^2 v_s^2}) \right\} dx \, dy \quad (7.47)$$

where  $J_0$  is the zero-order Bessel function. The integration over  $\varepsilon_s$  can be performed between 0 and infinity since L disappears if the condition (7.44) is not observed. Thus, we get

$$k = \frac{1}{4\pi^2} \int_{-\infty}^{+\infty} \frac{\cos(q_0 x)}{y^2} \left\{ \prod_{1}^{n} I_s(x, 0) - \prod_{1}^{n} I_s(x, y) \right\} dx dy \qquad (7.48)$$

where

$$I_{s}(x, y) = \int_{0}^{\infty} J_{0} \left[ \alpha_{s} \sqrt{\varepsilon_{s} \left( y^{2} + 4\pi^{2} x^{2} v_{s}^{2} \right)} \right] e^{-\varepsilon_{s}/kT} \frac{d\varepsilon_{s}}{kT} =$$

$$= \exp \left[ -\left( \frac{1}{4} \right) kT \alpha_{s}^{2} \left( y^{2} + 4\pi^{2} x^{2} v_{s}^{2} \right) \right]$$
(7.49)

If we make use of the definition of  $\alpha$ , then

$$k = \frac{1}{4\pi^2} \int_{-\infty}^{+\infty} \cos(q_0 x) \exp(-(1/4) kT \alpha^2 y^2) dy \int_{-\infty}^{+\infty} \left[1 - \exp(-kT \pi^2 \alpha^2 v_s^2)\right] \frac{dx}{x^2} =$$

$$= v \exp(-q_0^2/\alpha^2 kT)$$
(7.50)

where

$$v = \left(\sum_{1}^{n} \frac{\alpha_{s}^{2} v_{s}^{2}}{\alpha^{2}}\right)^{1/2}$$
 (7.51)

may be called the **weighted mean vibration frequency** for the molecule. It characterizes the vibrational state of the molecule as a whole. Since  $q_0/\alpha^2 = \epsilon_0$ , relation (7.50) may be represented in the form

$$k = ve^{-\varepsilon/kT} = ve^{-E/RT} \tag{7.52}$$

which can easily be compared with the simple Arrhenius equation. Evidently, v coincides with the pre-exponential factor A which has the dimensions of frequency, and  $E_0$ , i.e., the minimum energy required for the molecule to react, with the experimental activation energy.

The frequency of the reaction acts has been derived here as the time-averaged frequency. Figure 7.9 is an approximate representation of the change of the critical coordinate with time before and after an activating collision, which is described by Eq. (7.43). By definition, the reaction takes place when the curve q = f(t) intersects the  $q = q_0$  line upwards. Before a collision takes place the molecule has no sufficient energy distributed among the nu-

merous modes of vibration in such a manner that q reaches and exceeds  $q_0$ , in which case no reaction occurs. After the collision the curve intersects the line several times. The frequency of the reaction, L, is determined, for an individual molecule, by the number of such intersections in the positive direction per unit time. It must be clear that L is the frequency of the reaction for a given molecule with a given energy distribution; it should not be confused with v or A, which refer to a large assembly of molecules subject to a statistical treatment.

There are other derivations of the weighted mean frequency v, which give the same result and, possibly, are more directly associated with the problem under consideration and are therefore

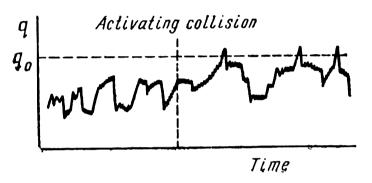


Fig. 7.9. The variation of the critical coordinate q in a molecule capable of unimolecular conversion before and after an activating collision.

more spectacular. Thus, for example, it has been shown that  $\mathbf{v}$  is equal to the ratio of the product of all the frequencies  $\mathbf{v}_s$  in a normal molecule to the product of the frequencies  $\mathbf{v}_s'$  when q is specified by any arbitrary value. Thus,

$$\mathbf{v} = \frac{\mathbf{v}_1 \mathbf{v}_2 \dots \mathbf{v}_n}{\mathbf{v}_1' \mathbf{v}_2' \dots \mathbf{v}_n'} \tag{7.53}$$

For the most important case—a reaction involving the rupture of the bond between atoms in a large molecule—the frequency factor v coincides in value with the vibration frequency of an imaginary diatomic molecule consisting of atoms the bond between which has the same force constant as the bond between atoms in a polyatomic molecule.

The above-considered variant of the theory assumes a simplified molecular model—a set of harmonic oscillators. This simplifying assumption is not of course rigorous since the vibrations in a general case are not small and, hence, are not harmonic. If this were so in actuality, the molecule would not be able to react.

The expression for v corresponding to the experimental factor A in the Arrhenius equation is written in the form (7.51)

$$\mathbf{v} = \left(\sum_{1}^{n} \alpha_{s} \mathbf{v}_{s}^{2} / \alpha^{2}\right)^{1/2}$$

and is, as was mentioned above, the weighted mean quadratic n of vibration frequencies in the reacting molecule. Therefore v must lie within the limits of ordinary vibration frequencies in the molecule, i.e.,  $10^{12}$  to  $10^{14}$  sec<sup>-1</sup>. The "normal" experimental value of the factor A is also within the same limits. The theory cannot

however account for the small frequency factors. Large A values can be explained if we assume a special distribution of vibration phases immediately after collisions.

The Slater theory gives an expression for the rate of reaction of molecules possessing an energy within the given limits, this expression resembling the one suggested by Kassel. The number of molecules with an intramolecular energy  $\sum \varepsilon_s$  ranging from  $\varepsilon$  to  $\varepsilon + d \varepsilon$ , is equal at equilibrium, according to Eq. (7.45), to

$$C_{\ell} d\varepsilon (\equiv C_{\ell})$$

where

$$\int_{\varepsilon} d\varepsilon = \int_{\varepsilon < \Sigma \varepsilon_{s} < \varepsilon + d\varepsilon} \dots \int_{\varepsilon} \int_{\varepsilon} (\varepsilon) d\varepsilon_{1} \dots d\varepsilon_{n} = \frac{\varepsilon^{n-1} e^{-\varepsilon/kT} d\varepsilon}{\Gamma(n) (kT)^{n}}$$

If  $Ck'_{\varepsilon}d\varepsilon$  equals the number of molecules having the indicated characteristic, which react per second, the overall rate constant will be written, according to Eq. (7.46), in the following form

$$k = \int k_{\varepsilon}' d\varepsilon = \int \dots \int L f(\varepsilon) d\varepsilon_1 \dots d\varepsilon_n$$

where  $k'_{\epsilon}$  is the contribution of molecules, the energy of which lies between  $\epsilon$  and  $\epsilon + d \epsilon$ .

Since the energy  $\varepsilon$  is expressed by the sum  $\sum \varepsilon_s$ , we have

$$\int_{0}^{\infty} k_{\varepsilon}' e^{-\varepsilon_{z}} d\varepsilon = (kT)^{-n} \int_{0}^{\infty} \dots \int_{0}^{\infty} L \exp\left\{-\left(Z + \frac{1}{kT}\right) \sum_{s} \varepsilon_{s}\right\} d\varepsilon_{1} \dots d\varepsilon_{n} =$$

$$= v \left(1 + ZkT\right)^{-n} \exp\left\{-\varepsilon_{0}\left(Z + \frac{1}{kT}\right)\right\}$$

where the integration is carried out by the method used above. Having written  $\varphi(Z)$  for the last expression, we obtain the following through the use of the Laplace transform:

$$k_{\mathbf{\epsilon}}' = \frac{1}{2\pi i} \int_{C-i}^{C+i\infty} \varphi(Z) e^{\varepsilon_{\mathbf{z}}} dZ \qquad (C \geqslant 0)$$

the solution of which leads to the following value of the constant for the given energy interval:

$$k_{\varepsilon}' = \frac{ve^{-\varepsilon \cdot kT} \left(\varepsilon - \varepsilon_0\right)^{n-1}}{\Gamma(n) \left(kT\right)^n} \left(\varepsilon > \varepsilon_0\right)$$

$$k_{\varepsilon}' = 0 \quad \left(\varepsilon < \varepsilon_0\right)$$
(7.54)

Now we can write the rate constant for molecules whose energy lies between the limits  $\varepsilon$  and  $\varepsilon + d \varepsilon$ ;

$$k_{\varepsilon} = \frac{k_{\varepsilon}'}{l_{\varepsilon}} = v \left(\frac{\varepsilon - \varepsilon_0}{\varepsilon}\right)^{n-1} \quad (\varepsilon > \varepsilon_0)$$
 (7.55)

This expression is formally identical with the expression derived by Kassel in his classical theory—Eq. (7.37). In the Kassel theory, the factor  $[(\varepsilon - \varepsilon_0)/\varepsilon]^{s-1}$  expresses the probability that of the total energy  $\varepsilon$  distributed among s equivalent classical oscillators, the amount  $\varepsilon_0$  will be concentrated on one "critical" oscillator.

The Slater theory furnishes a method for calculating the preexponential factor of the Arrhenius equation for a unimolecular reaction on the basis of the properties of a normal unexcited moiecule. The advantage of this theory over other theories consists in that, with account taken of the vibrational characteristics of the molecule, it can predict, without additional arbitrary assumptions, that molecules having a higher energy content must react more rapidly than those possessing the energy minimum required for the reaction to take place. True, the last-named proposition concerning the dependence of the rate of conversion of molecules on energy content above the minimum energy has not yet been verified by direct experiments, but it is thought to be rational and has been repeatedly confirmed indirectly. The Kassel theory too adopts this dependence but it does not provide a method of calculating the constant v, which in this case determines the frequency of exchange of energy between the oscillators. In view of this, for a numerical agreement between theory and experiment to be obtained, the quantity v is equated to the experimental factor A.

In the Slater theory, just as in a number of other theories, the rate of activation is found by calculating the equilibrium concentration and the rate of deactivation on the assumption of the efficiency of each collision. The "population" of any energy region  $(\varepsilon_s, \varepsilon_s + d \varepsilon_s)$  (s = 1, 2, 3, ..., n), when the set of individual values of  $\varepsilon_s$  satisfy condition (7.44), will be expressed at equilibrium as follows:

$$Ce^{-\epsilon/kT}\prod \frac{d\epsilon_s}{kT}, \quad \epsilon = \sum_{1}^{n} \epsilon_s$$

In writing this and the subsequent relations, use is naturally made of the symbols that have already been employed. The collision frequency for molecules and, hence, the rate of deactivation, is written in an ordinary form:

$$\omega = ZC, \quad Z = 2D^2 \left(\frac{\pi kT}{m}\right)^{1/2}$$

Accordingly, the number of molecules which acquire energy values within the indicated limits per unit time will be given by

$$\omega C e^{-\epsilon/kT} \prod (d\epsilon_s/kT)$$

However, the number of activated molecules with an energy in any interval of its values will be, because of their disappearance in the course of the reaction, somewhat lower than that in accordance with the Boltzmann distribution law, say, Cg ( $\varepsilon_1$ ,  $\varepsilon_2$ , ...,  $\varepsilon_n$ )  $d\varepsilon_1$ ,  $d\varepsilon_2$ , ...,  $d\varepsilon_n$ , the quantity g being subject to determination.

The number of molecules reacting per unit time will be now given by

$$CgLd\varepsilon_1 \dots d\varepsilon_n$$
 (7.56)

and the number of molecules being deactivated will be

$$\omega Cg d\varepsilon_1 \dots d\varepsilon_n$$
 (7.57)

In the stationary state, the number of molecules being activated by collisions is equal to the number of deactivated and reacting molecules. Hence, we have the following relation

$$(L + \omega) g = \omega e^{-\varepsilon/kT} (kT)^{-n}$$
(7.58)

which makes it possible to determine g. Integration of Eq. (7.56) over the energies of the internal degrees of freedom gives the rate constant for a unimolecular reaction

$$k = -\frac{1}{C} \cdot \frac{dC}{dt} = \int \dots \int gL \, d\varepsilon_1 \dots d\varepsilon_n$$

Replacing g by its value from Eq. (7.58), we get the expression

$$k = \int \dots \int \frac{Le^{-\varepsilon/kT}}{1 + L/\omega} \prod_{1}^{n} \left(\frac{d\varepsilon_{s}}{kT}\right)$$
 (7.59)

in which the integration is extended over the region of energy values corresponding to the activated state.

In view of the mathematical difficulties, the exact mathematical expression for L cannot be used for further development of the theory. In place of the exact expression, according to Slater, use is made of a simple approximate expression:

$$L = \frac{1}{[(1/2) n - 1/2]!} \left( \frac{\sum |a_s| - q_0}{2\pi} \right)^{\frac{1}{2}(n-1)} \left( \frac{\sum |a_s| v_s}{|a_1 a_2 \dots a_n|} \right)^{\frac{1}{2}}$$
(7.60)

Then, if only  $b \equiv \epsilon_0/kT$  is great and the values of  $\mu$  determinable by the relation

$$\mu = \frac{|\alpha_s|}{\alpha} \left( \sum \mu_s^2 = 1 \right)$$

and the frequencies v are not scattered widely, we can find the n-fold integral of relation (7.59). The following expression for the rate constant is obtained:

$$k = ve^{-b}I_n(\theta) \tag{7.61}$$

where

$$\frac{k}{k_{\infty}} = I_n(\theta) = \frac{1}{\left[\frac{1}{2}n - 1/2\right]!} \int_0^{\infty} \frac{x^{\frac{1}{2}(n-1)}e^{-x} dx}{1 + x^{\frac{1}{2}(n-1)}\theta^{-1}}$$
(7.62)

In its turn, in formula (7.62) the following notations are adopted:

$$x = (\varepsilon - \varepsilon_0)/kT \tag{7.63}$$

$$\theta = (\omega/v) b^{\frac{1}{2}(n-1)} f_n \tag{7.64}$$

$$f_n = (4\pi)^{\frac{1}{2}(n-1)} \left( \frac{1}{2} n - 1/2 \right)! \mu_1 \mu_2 \dots \mu_n$$
 (7.65)

At high pressures  $\omega$  and  $\theta$  tend to infinity and  $I_n(\theta)$  tends to unity, so that the rate constant approaches the limiting value with increasing pressure, as should be expected.

At low pressures  $\omega$  and  $\theta$  tend to zero, and the expression for the constant k assumes the form

$$k \simeq ve^{-b} 0 / (\frac{1}{2} n - 1/2)! = \omega \mu_1 \mu_2 \dots \mu_n (4\pi b)^{\frac{1}{2} (n-1)} e^{-b}$$

which results from the use of only the first term of the more exact formula

$$k = \omega \mu_1 \mu_2 \dots \mu_n (4\pi b)^{\frac{1}{2}!(n-1)} e^{-b} \left\{ 1 - {n-1 \choose 2} \frac{1}{2b} + 1 \times 3 {n-1 \choose 4} \frac{1}{2b^2} \dots \right\} = \omega \Lambda$$
 (7.66)

which was derived by Slater.

These formulas, just as the Slater theory as a whole, are based on the concept of a molecule as a set of simple harmonic oscillators and also on the condition (7.44) of the activated state of the molecule. As has been found, a molecule with an energy greater than  $\varepsilon_0$  but distributed in contrary to condition (7.44) has a certain chance to react if left to itself for a long time. Of course, the reaction can occur if the transfer of energy from one mode of vibration to another is not absolutely forbidden, as required by the strictly "harmonic" model. The vibrations in a molecule are not, as a matter of fact, strictly harmonic, so that a certain migration of energy will take place. No method of calculating the pos-

sible velocity of this type of migration has been devised yet. But it is still possible to estimate approximately the effect of, so to say, the completely free migration on the velocity predicted for a low pressure. It should however be noted that the velocity calculated in this way coincides with that obtained from the Kassel theory. According to this theory, as is already known, all molecules having an energy in excess of  $\varepsilon_0$  and left to themselves for a sufficiently prolonged period of time will enter into reaction. As an example of the assessment of the above-mentioned effect for a molecule in which all the  $\mu$ 's are the same, and  $b = \varepsilon_0/kT = 40$ , Slater gives the following values of  $k/\omega = \Lambda e^b$ :

			n = 1	3	5	7	9	13
` '	condition observed	(7.44)	1		10 <sup>3.6</sup>		$10^{6.2}$	108.5
(b) if	condition	$\epsilon \equiv \epsilon_0$						
is	sufficient		1	$10^{2.9}$	$10^5$	$10^{6.8}$		

As has already been mentioned, the rate of transfer of energy from one mode of vibration to another is unknown. But, apparently, at a certain pressure characteristic for a given molecule, such a transfer must occur and this will be reflected in the value of the ratio  $k/k_{\infty}$  in accordance with the transition from the limiting condition (a) to condition (b).

There are, however, no sufficiently accurate data on the observation of this effect over a wide pressure range. Detection of the effect would be of great importance for the confirmation of the Slater theory.

For intermediate pressures, between the regions of realization of pure I and pure II orders there can be carried out a numerical integration of  $I_n(\theta)$  [relation (7.62)]. Strictly speaking, for each of the molecules under study there must be made separate calculations on substitution of the corresponding values of  $\mu_s$ , m, D, n, etc. But, as has been found for three rather typical molecules, for which the critical coordinate  $q_0$  is the distance between carbon and hydrogen atoms, the series  $\mu_1, \mu_2, \ldots, \mu_n$  is a geometrical progression,  $\mu_1$  being equal to  $5\mu_n$ . An approximate calculation has been performed for such typical molecules having a molecular weight of 50, the collision diameter 5 Å, the frequency v ==  $10^{13.7}$  sec<sup>-1</sup>, b = 40 and at a temperature of 700 K. The results of these calculations for various values of n are presented in Fig. 7.10 as plot of the rate constant versus the logarithm of pressure. As can be seen from Fig. 7.10, the change of n affects, in the first place, the position of the curve relative to the abscissa. The lower the value of n the higher the pressures at which the

limiting value of the constant is reached. The shape of the curve varies relatively little, which can be tested only if the accuracy of experimental data is very high.

If n=1, the integral (7.62) is determined accurately. Namely, we find that

and

$$I_{1}(\theta) = 1/(1 - \theta^{-1}), \quad \theta = \omega/\nu$$

$$\frac{k}{k_{\infty}} = \frac{1}{1 + \frac{\nu}{\omega}}$$

This expression coincides exactly with the expression derived for

Loy ko 0.0 -0.5 -1.0 -1.5 -2.0 - 2.5 G

Fig 7.10 The rate constant of a unimolecular reaction versus the initial pressure for molecules of various degrees of complexity, according to the Slater theory, at n ranging from 3 to 13

The dotted line shows the slope tor a bimolecular process

all molecules in the Lindemann theory:

$$\frac{k}{k_{\infty}} = \frac{1}{1 + \frac{k_2}{k_3 [\Lambda]}} \tag{7.67}$$

so that the curves for n = 1and for the Lindemann theory coincide. Since, probably, for a very limited number of molecules n < 5, we can easily distinguish the Lindemann-Hinshelwood from the curves obtained in other, more developed theories. The shapes of experimental curves are usually determined with an accuracy sufficient for the establishment of such a difference. As

has already been said, the Lindemann-Hinshelwood theory cannot provide a quantitative explanation for the dependences observed in experiments. This failure should probably be ascribed to the neglect of the relationship between the reactivity of molecules and the excess energy. Thus, it turns out that the Lindemann-Hinshelwood theory predicts the same shape (but not the same position) for the  $\log k/k_{\infty}$  vs.  $\int (\log p)$  curves for all molecules, no matter how complex they are.

The discrepancy between the predictions of the Lindemann-Hinshelwood theory (the HL theory) and experiment and also the Slater theory can be shown once again with the aid of the graph of 1/k vs. 1/p. The Lindemann-Hinshelwood theory predicts a straight line. The Slater theory is seen to be able to describe an experimental curve (Fig. 7.11).

Other theories of unimolecular reactions that deserve mention, namely the Rice-Ramsperger-Kassel theories (known as the RRK theories), proceed from the basic assumption that the lifetime of a molecule is reduced as its energy increases. Both in the classical and quantum versions of the Kassel theory it is assumed that a molecule attains a critical state when the requisite amount of energy is concentrated on the corresponding separate oscillator.

According to Rice and Ramsperger, such a concentration of energy takes place in a single quadratic term. The differences in

both theories stem precisely from these nuances of the main assumptions. In the classical Kassel theory, the frequency of possible conversions of a molecule possessing an energy E is given by relation (7.37), where s is the number of "active" oscillators in the molecule; this expression is formally identical with that derived in the Slater theory, (7.55). From relation (7.37) there is obtained the following expression for the ratio  $k/k_{\infty}$ :

$$\frac{k}{k_{\infty}} = \frac{1}{(s-1)!} \int_{0}^{\infty} \frac{x^{s-1}e^{-x} dx}{1 + \frac{A}{\omega} \left(\frac{x}{b+x}\right)^{s-1}}$$
(7.68)

But, even leaving out the question of the validity of this or that molecular model, it should be noted that these theories are considerably less satisfactory than Slater's theory. First, in the RRK theories the number of active oscillators is not determined theoretically; it is chosen so as to obtain agreement between predictions

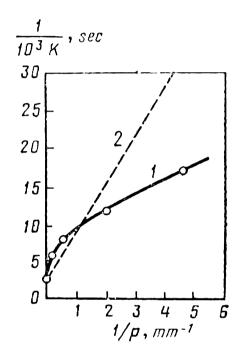


Fig. 7.11. The variation of the rate constant of the isomerization of cyclopropane with pressure:

1—experimental curve; the points have been calculated according to Slater; 2—curve corresponding to the Lindemann theory.

and experimental evidence. Second, these theories employ preferentially the pre-exponential factor A found by experiment than the frequency calculated on the basis of a molecular model, whereas the Slater theory makes use of only one experimental quantity determined from kinetic data—the energy of activation. Owing to the similarity between Eqs. (7.63) and (7.68) the  $\log k/k_{\infty} = f(\log p)$  curve in the Kassel theory has the same shape as in the Slater theory if

$$n = 2s - 1$$

but, though A and  $\nu$  may be equal, the curves do not coincide in a general case.

In connection with the Slater theory it should be emphasized

that v and p are conjugate quantities and  $E_0$  and T are approximately conjugate quantities, not only because  $T^{1/2}$  is contained in the expression for the rate of deactivation  $\omega$  and, hence, in  $\theta$ .

Slater derived an approximate expression which describes the displacement of the  $\log k/k_{\infty}$  curve with temperature. According to Eq. (7.64), for a given gas the ratio  $k/k_{\infty}$  is proportional to the quantity  $pb^{1/2(n-1)}T^{-1/2}$ , i.e.,  $pT^{-1/2n}$ . Hence, the ratio  $k/k_{\infty}$  assumes the same value for the pairs p and T, for which  $pT^{-1/2n}$  is constant. As a result, the curve corresponding to a lower temperature  $T_1$  will be shifted relative to the curve corresponding to  $T_2$  by the amount

$$\Delta \log p = \frac{1}{2} n \log \frac{T_2}{T_1} \tag{7.69}$$

This conclusion is in accord with the intuitive expectation that at higher temperatures the same fall-off of the rate will occur at higher pressures. For this relationship to be tested, however, there are no sufficiently accurate experimental evidence yet.

Let us now turn, for a while, to a bimolecular reaction which is assumed here to be the reverse of a unimolecular reaction:

$$A \underset{k_2}{\overset{k_1}{\Longleftrightarrow}} B + C$$

The rate constants for such reactions are interrelated by the equilibrium constant,  $K = k_1/k_2$ , which is independent of temperature. Therefore,  $k_2$  decreases at low pressures, just like  $k_1$ , and

$$\frac{k_1}{k_{\perp(\infty)}} = \frac{k_2}{k_{2(\infty)}}$$

Hence, in principle, the decline of the rate constant of a unimolecular reaction with pressure can be established by investigating (if it is more convenient) the bimolecular reaction experimentally. The converse is also true: the rate constant of a bimolecular reaction depends on pressure (at sufficiently low p values) since the primary act of association involves the formation of a molecule with an energy sufficient for dissociation to occur. It must be stabilized by a collision, which removes part of the energy. In some cases it is simpler to study a unimolecular reaction, and in other cases, a bimolecular reaction, but the exact theoretical treatment of unimolecular reactions is always simpler since no satisfactory method of calculating the frequency of ternary collisions has been developed up to the present time. On the other hand, it is usually possible to measure or calculate the corresponding equilibrium constant and therefore the problem of association may, so to say, be "reversed".

The energy of activation is determined by the Arrhenius equation

$$E = RT^2 \frac{\partial \ln k}{\partial T}$$

and therefore the energy of activation  $E_p$  for unimolecular reactions of the Slater model of the molecule at very low pressures

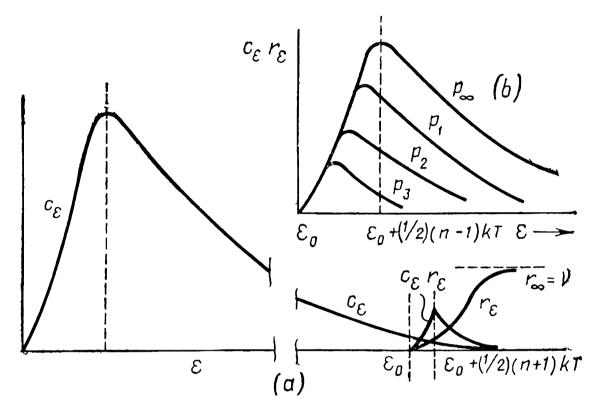


Fig. 7.12. The distribution of molecules among the energy levels (a).

The contribution of molecules of given energy to the overall reaction rate  $[c_{\epsilon}]$  is the fraction (concentration) of molecules having energy within the range  $\epsilon$  to  $\epsilon+1$ ;  $r_{\epsilon}$  is the average rate constant of the reaction of such molecules; (b)—part of Fig. a, showing the decrease of the overall rate (and of activation energy) with decreasing pressure. The pressure  $P_{\infty}$  is the limiting value:  $P_1 > P_2 > P_3$ .

will be defined with the aid of Eq. (7.66) as follows:

$$E_p = RT^2 \frac{\partial \ln \omega}{\partial T} + RT^2 \frac{\partial \ln \Lambda}{\partial T}$$
 (7.70)

Experiments are often carried out at constant pressure when  $\omega$  is proportional to  $T^{-1/2}$  since the first term in Eq. (7.70) gives  $-\frac{1}{2}RT$ . To determine the second term, we write  $b=E_0/RT$ . Then

$$RT^2 \frac{\partial \ln \Lambda}{\partial T} = -E_0 \frac{\partial \ln \Lambda}{\partial b}$$

Hence, taking account of Eq. (7.66), we can express the second term of Eq. (7.70):

$$E_0 - \frac{1}{2}(n-1)RT\left\{1 - {n-1 \choose 2}\frac{1}{2b} + \dots\right\} / \left\{1 - {n-1 \choose 2}\frac{1}{2b} + \dots\right\}$$

Further, neglecting all the terms in braces, except the first one in parenthesis, we get

$$E_0 - \frac{1}{2} (n-1) RT$$

and

$$E_{p} = E_{0} - \frac{1}{2} n \left( RT \right)$$

The cause of such a decrease in the energy of activation upon approach to the second-order region is clear from Fig. 7.12. On the left part (a) is schematically shown the distribution of energy among molecules and also their contribution to the overall rate of the reaction. The right part (b) shows a gradual decrease of the contribution of molecules having an increased energy with decreasing pressure and, as a consequence thereof — the decrease of the observed energy of activation (the peak on the curve of the product  $C_{\epsilon}r_{\epsilon}$  is shifted to the left). Indeed, there is evidence indicating the decrease of the activation energy of a unimolecular reaction with decreasing pressure.

## 7.4. Termolecular Reactions

The theory of termolecular reactions is perhaps the least developed, possibly because among ordinary gas reactions their number is very limited. In particular, reactions involving nitric oxide, for example,

$$2NO + O_2 \longrightarrow 2NO_2$$

and other similar reactions are sometimes classified as termolecular reactions.

That the reaction is third order overall, second order in nitric oxide and first order in oxygen (and also in chlorine and bromine) may, however, be accounted for, without reference to a triple collision, by postulating the existence of the dimer (NO)<sub>2</sub> or the complex NO<sub>3</sub>. The simplest approach is to assume (just as was done in Sec. 2.3) the equilibrium concentration of the dimer proportional to the square of the concentration of NO. On the whole, the third order obtains. The same scheme may be expected to account also for the temperature coefficient of the reaction (7.71), which is smaller than unity, provided that we assume the exothermicity of the dimer formation. However, difficulties arise immediately in this connection, which are associated with the question whether the dimer formation itself requires a ternary collision.

Here we shall discuss the simple collision theory of termolecular reactions, which is based on the number of ternary collisions. This number has been calculated above (see Chapter 6) and writ-

TABLE 7.8. The Arrhenius Constants for Selected Termolecular Reactions

Reaction	Pre-exponential factor log A, litre 2.mole 2.sec 1	Energy of activation, keal/mole	Steric tactor P
i. $2NO + O_2 \rightarrow 2NO_2^*$	3.02	-1:1	ca. 10 <sup>-7</sup>
2. $2NO + Cl_2 \rightarrow 2NOCI *$	3.66	3.7	ca. 10 <sup>-6</sup>
$3. 2NO + Bt_2 \rightarrow 2NOBr *$	3.50	0 (3)	ca. 10 <sup>-6</sup>
4. $2NO_2 + M \rightarrow N_2O_4 + M$ ( $M \equiv N_2$ at 1 atm. 25°C)	6.50	2.3	ca. 10 <sup>-+</sup>
5. $H + H + M \rightarrow H_2 + M$	10.0	0 (3)	ca. 1
6. $H + O_2 + M \rightarrow HO_2 + M \ (M \equiv H_2)$ $(M = O_2)$	7 1 8.1	0 (?)	ca. $10^{-3}$
7. Br + Br + M $\rightarrow$ Br <sub>2</sub> + M ( $M \equiv \text{He, H}_2, \text{ N}_2, \text{ CH}_4, \text{ CO}_2, \text{ Ar}$ )	9.6	0 (?); -1.5 (Ar)	ca 0.4
8. $I + I + M \rightarrow I_2 + M$ $(M \equiv I_2)$ $(M \equiv He, Ar, H_2, n\text{-butane})$ $(M \equiv n\text{-}C_6H_{12}, \text{ tetramethylmethane, } N_2, CH_4, CO_9)$	7.8 9.57 10.50	-4.4 0 (?); -1.7 (butane) 0 (?)	ca. 10 <sup>-2</sup> ca. 0.3 ca. 1
(M≡mesitylene, benzene)	11.45	(¿) 0	ca. 1
9. $O + O_2 + M \rightarrow O_3 + M$ $(M \equiv O_2, O_3, CO_2, N_2, He)$	7.54	9.0—	ca. 10 <sup>-</sup> .
10. $O + NO + M$ (?) $\rightarrow NO_2 + M$ (air) 11. $O + NO_2 + M$ (?) $\rightarrow NO_3 + M$ (air)	10.3	0 (?) ? ?	
27.7 - 27 27 7 7 7 7 7	- 8.8 - 1	(¿) O	ca. 0.4

For the first three reactions, the possibility of the occurrence of a more complicated mechanism involving the formation of an intermediate complex is not excluded.

ten in the form:

$$Z_{123} = 8 \sqrt{2} \pi^{3/2} D_{12}^2 D_{23}^2 \delta (kT)^{1/2} \left\{ \frac{1}{\mu_{12}^{1/2}} + \frac{1}{\mu_{23}^{1/2}} \right\} n_1 n_2 n_3$$
 (7.71)

The rate of the reaction, by analogy with bimolecular reactions, is written in the following form:

$$\mathbf{w} = PZ_{123}e^{-E/RT} = PZ_{123}^0e^{-E/RT}n_1n_2n_3$$

Here P is the steric or probability factor, and

$$Z_{123}^{0} = 8 \sqrt{2} \pi^{3/2} D_{12}^{2} D_{23}^{2} \delta (kT)^{1/2} \left\{ \frac{1}{\mu_{12}^{1/2}} + \frac{1}{\mu_{23}^{1/2}} \right\}$$
(7.72)

will express the frequency factor equal to the number of collisions at unit concentrations.

For the purposes of an approximate comparison of theory with experiment we shall simplify Eq. (7.73), setting the molecular masses equal to one another, i.e.,  $m_1 = m_2 = m_3 = m$ , and also their linear dimensions, i.e.,  $D_{12} = D_{23} = D$ . We get

$$Z_3^0 = 178D^4 \delta \left(\frac{RT}{M}\right)^{1/2} \tag{7.73}$$

where R is the gas constant and M is the molecular weight.

If we assume, for example, that  $D = 3 \times 10^{-8}$  cm,  $\delta = 10^{-8}$  cm, M = 30 and M = 30 K, then at  $M = 8.3 \times 10^{7}$  erg·deg<sup>-1</sup>. mole<sup>-1</sup>: M = 20 cm<sup>6</sup> molecules<sup>-2</sup>·sec<sup>-1</sup> = 1.49 × 10<sup>10</sup> litres<sup>2</sup>·mole<sup>-2</sup>·sec<sup>-1</sup>

Hence,  $\log Z_3^0 = 10.17$  and, if reference is made to Table 7.8, it will turn out that the thus calculated frequency factor corresponds almost exactly to the most rapid termolecular reactions with the participation of atoms (reactions 5, 7, 8, 10, 11, and 12). This excellent agreement between calculations and experiment means that the steric factor is equal to unity and the energy of activation to zero, which might be supposed to lead to the efficiency of every collision. In a number of cases, however,  $\log A$  proves to be considerably lower than  $\log Z_3^0$ . In such cases, considering, as before, that E=0, one may formally introduce the steric factor P (the last column in Table 7.8). For the first three reactions, which belong to the category of ordinary chemical reactions, the steric factor is found to be very small ( $10^{-7}$  to  $10^{-6}$ ) and this is difficult to explain within the framework of the theory under discussion if no recourse is made to a complicated mechanism. The point is probably that these reactions are not termolecular reactions and proceed, at least, in two consecutive steps.

# The Activated-Complex Theory (Transition-State Theory)

### 8.1. Potential-Energy Surfaces

The basic idea of the **transition-state theory** (also known as the *activated-complex theory*)\* consists in that in the course of any chemical reaction the initial configuration of atoms turns into the final configuration as the result of the continuous change of the internuclear distances. To begin with, we shall consider the reaction between an atom X and a diatomic molecule YZ, i.e., the following reaction

$$X + YZ \longrightarrow XY + Z$$

As can be shown, this reaction is accomplished most simply, i.e., with the least consumption of energy, if the atoms are arranged along the line connecting their centres. Then the course of the reaction may be described by using only two interatomic distances,  $r_1$  and  $r_2$  (Fig. 8.1);  $r_1$  decreases and  $r_2$  increases. In the

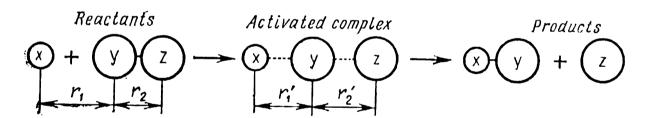


Fig. 8.1. The reaction between an atom and a diatomic molecule occurs by way of a continuous variation of the internuclear distances.

course of this continuous and simultaneous variation of interniclear distances (bond lengths) there is always formed a certain intermediate configuration  $X\cdots Y\cdots Z$ , in which the Y-Z bond has already been weakened but not completely broken, and the X-Y bond is in the process of being formed. In this configuration the atom Y simultaneously belongs, so to say, to the atom X and the atom Z. Such a configuration is critical for the given reaction: the reaction products may appear only on the condition of the formation of this configuration, which is called the **transition state** or the **activated complex**.

As is shown by experiment and calculations, the alteration of internuclear distances entails the change of the potential energy

<sup>\*</sup> The transition-state theory is sometimes referred to as the theory of absolute reaction rates or, simply, as absolute rate theory.—Tr.

of the system because, for example, upon approach of the atom X to the molecule YZ the atom has to overcome the forces of repulsion of the electron shells. Properly speaking, the determination of the function  $U = f(r_1r_2)$  is the determination of the activation energy of the reaction. In principle, the potential energy of a triatomic system, as related to  $r_1$  and  $r_2$ , can be calculated theoretically, using, for example, the so-called London equation:

$$U_{r_1r_2} = A + B + C - \left\{ \frac{1}{2} \left[ (\alpha - \beta)^2 + (\beta - \gamma)^2 + (\gamma - \alpha)^2 \right] \right\}^{1/2}$$
 (8.1)

which allows the interaction in the triatomic system to be replaced by the interaction of three diatomic molecules. Thus, A represents the Coulomb interaction in molecule XY and  $\alpha$  the exchange interaction in the same molecule. So,  $A + \alpha$  expresses the total bond energy in molecule XY. The symbols B and C and also  $\beta$  and  $\gamma$  denote the corresponding quantities in the molecules YZ and XZ.

Incidentally, the complete theoretical calculation of the function  $U=f(r_1r_2)$  remains to be, up to the present time, a mere possibility because of extremely formidable mathematical difficulties and the actual calculation can be carried out by means of the semi-empirical method proposed by Eyring. The total bond energy in a diatomic molecule,  $A+\alpha$ , is taken from experimental data. Use is conveniently made here of the Morse empirical function \*, which is known to express the dependence of the energy of a diatomic molecule on the internuclear distance. For example, for the molecule XY:

$$U_{(r)} = A + \alpha = D_e \left[1 - e^{-a(r-r_e)}\right]^2$$

In this formula,  $D_c = D + 1/2\hbar v$  is the energy of dissociation plus the vibrational zero-point energy of the molecule,  $r_c$  is the equilibrium interatomic distance, and a is a constant characterizing the given molecule. These quantities are all found from spectroscopic data. If they are known for all the three molecules, XY, YZ, and XZ, then, using the Morse equations, one can determine the total energies  $A + \alpha$ ,  $B + \beta$ , and  $C + \gamma$  for all the interatomic distances in the system X···Y···Z. For calculations to be performed by means of the London equation, it is necessary to know the values of the Coulomb and exchange components separately. For these to be determined, it is assumed, as suggested by Eyring, that the Coulomb interaction for all the distances is a certain constant fraction of the total bond energy (usually, 15-20 per cent). In this way it is possible to calculate  $U = \int (r_1 r_2)$  for the triatomic system under consideration and to present the results of the cal-

<sup>\*</sup> See also Chapter 5 (Sec. 5.10) where the graph of this function is given.

culations in the form of a potential-energy surface.\* This three-dimensional surface is most conveniently represented on a two-dimensional diagram by the contour-line method adopted in orography. Namely, this surface is cut by equidistant horizontal planes and the cross-section contours are projected onto the plane. An example of the potential-energy contour map constructed in this manner is presented in Fig. 8.2, where the contour lines are

drawn through every 10 and 5 kcal/mole. Obviously, the density of arrangement of the contour lines points to the steepness of the slope of the surface. In fact, two deep "valleys" can be distinguished on the surface, these valleys being separated by a relatively low "mountain pass". The upper left-hand part of the surface (large  $r_1$  and small  $r_2$ ) corresponds to the initial system for the reaction, i.e., to the molecule YZ and the atom X which does not interact with the molecule. Here the profile of the vertical cross-section of the surface will express the dependence of the potential energy of the molecule

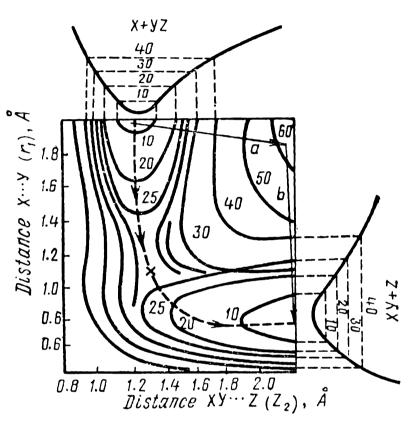


Fig. 8.2. A potential-energy surface map for the reaction between an atom and a diatomic molecule:

The dotted line is the reaction path (the reaction coordinate); the cross is the saddle point.

YZ on the distance  $r_2$  (curve 1). The lower right-hand part of the surface corresponds to the reaction products XY + Z. Here the profile of the vertical cross-section expresses  $U = f(r_1)$  for the molecule XY. Besides, there is a flat plateau in the upper right-hand part of the potential-energy surface. It corresponds to three free, i.e., non-interacting, atoms separated by sufficiently large distances.

Perhaps, the easiest way for the system to get from the initial to the final state is to travel along the floor of one of the valleys (the entrance valley or channel) over the mountain pass and, farther, along the floor of the other valley (the exit valley or channel). Other paths are also possible, of course, but they will

<sup>\*</sup> In the same way as for a diatomic molecule U = f(r) and is expressed by means of a plane curve.

all be associated with a greater consumption of energy. For example, we can visualize the initial dissociation of the molecule YZ into free atoms with the subsequent recombination of X and Y. This would mean the initial rise of the reacting system to the flat plateau with the subsequent descent into the valley of the products \* (called the exit valley or channel). The energy  $\Delta E$  required for this to occur would, however, be considerably higher—the plateau is situated much higher than the mountain pass between the valleys. The probability of this or that process (and

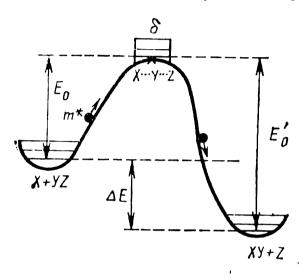


Fig. 8.3. The energy profile of the reaction path:

 $E_{-}$  is the activation energy of the forward reaction;  $E_{0}'$  is the activation energy of the reverse reaction;  $\Delta E$  is the reaction heat.

the rate of its progress) is proportional to the factor  $\exp(-\Delta E/RT)$ , which decreases very rapidly with Therefore, in increasing  $\Delta E$ . overwhelming majority of cases, the reaction is effected by the route of the least energy consumption; it is designated by a dashed line Fig. 8.2 and is called the reaction path or the reaction coordinate. The highest point of this reaction coordinate—the mountain pass or the energy barrier (marked by an X) with the coordinates  $r'_1$  and  $r'_2$ —corresponds apparently to the transition state or activated complex since only when this point has been reached can the system begin descending into the

(exit) valley of the products XY + Z. For more clarity, we can flatten out the reaction coordinate into a straight line and lay off the portions of this path along the abscissa and plot the heights or energies corresponding to the path points along the ordinate. Then a curve with a maximum is obtained, which may be called the energy profile of the reaction path (Fig. 8.3). The point of the maximum—the so-called saddle point (the top of the energy barrier)—corresponds, as has already been said, to the transition state  $X \cdots Y \cdots Z$ . The height of the maximum, or the energy difference between the zero vibrational levels of the transition state and reactants,  $E_0$ , is the energy of activation, i.e., the energy minimum required for the transition state (activated complex) to be formed from the reactants. Since the difference between the zero levels is taken, the energy of activation should be regarded as being referred to the absolute zero.

In connection with Fig. 8.3 we may also note the following. For the reverse reaction

$$XY + Z \longrightarrow X + YZ$$

<sup>\*</sup> This path is marked by two arrows (a and b).

the transition state will have the same configuration as for the forward reaction, only the reaction coordinate must be counted off in the opposite direction. The activation energy of the reverse reaction will be  $E_0'$  and the quantity  $\Delta E$  will represent the heat of the reaction, which is thus equal to the difference in activation energy between the forward and reverse reactions.

The construction of a multidimensional potential-energy surface is thus intended to solve a number of important problems and, in the first place, shows the fundamental way to a theoretical calculation of the activation energy (though this way is not yet practically available because of the mathematical difficulties involved). Secondly, the position of the saddle point on the potential-energy surface gives directly the internuclear distances in the transition state of the system,  $r'_1$  and  $r'_2$ . Moreover, the configuration of the saddle could provide information on the vibrational characteristics of the transition state if the potential-energy surface were constructed accurately.

All these data are necessary for a complete theoretical calculation of the reaction rate and the construction of the potential-energy surface is the first step in this calculation.

Thus, there appears the possibility of developing a theory that will allow the rate of a reaction to be theoretically calculated on the basis of the properties of the reactant molecules—the **theory of absolute reaction rates.** This possibility, however, remains, up to now, a mere possibility since the complete calculation, including the determination of the activation energy, can be carried out, and even then approximately, in the simplest cases, for example, in the following exchange reaction

$$D + H_2 \longrightarrow DH + H$$

Nonetheless, even the mere possibility is a step forward since what remains to do is to cope with the mathematical difficulties involved. More significant are the advances achieved by the transition-state theory as regards the calculation of the pre-exponential factors A in the Arrhenius equation.\*

#### 8.2. Statistical Calculation of Reaction Rates

We have resorted earlier to a mechanical analogy (see Sec. 2.3) in describing the interconversions of the kinetic and potential energies in a diatomic molecule, which are analogous to the transformations of the energies of a heavy material particle sliding without friction in the field of the gravity force along a trough simulating the profile of the potential-energy curve. In

<sup>\*</sup> See Chapter 8 (Sec. 8.3).

this case too it is useful to resort to the same analogy by visualizing a particle having a certain effective mass  $m^*$  and sliding along the potential-energy surface. With the appropriate selection of the effective mass, the interconversions of its kinetic and potential energies will simulate the corresponding conversions in the triatomic system under consideration. The effective mass  $m^*$  should not be confused with the mass of the transition state (the activated complex); this is an auxiliary quantity which depends, for example, on the intensity of the gravity force. The final calculation results do not contain  $m^*$ . For the sake of rigour it

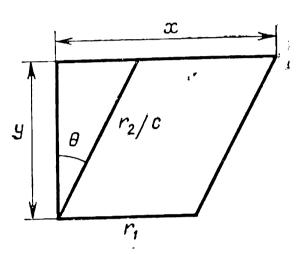


Fig. 8.4. Construction of the potential-energy surface in oblique coordinates.

should also be pointed out that for a more precise concordance to be obtained between the energy conversions for the particle  $m^*$  and the triatomic reacting system, the values of  $r_1$  and  $r_2$  should be plotted along the axes of oblique coordinates in constructing the potential-energy surface (Fig. 8.4). As can be shown, the following relationships must be satisfied:

$$r_1 = x - y \tan \theta \tag{8.2}$$

$$r_2 = Cy \sec \theta \tag{8.3}$$

where x and y are the rectangular coordinates corresponding to  $r_1$  and

 $r_2$ , and C is a constant. It can also be shown (we shall not dwell on the details here) that the constant C and the angle  $\theta$  depend on the masses of the three particles which make up the system. Namely,

$$C = \left[ \frac{m_1 (m_2 + m_3)}{m_3 (m_1 + m_2)} \right]^{1/2}$$

$$\sin \theta = \left[ \frac{m_1 m_3}{(m_1 + m_2) (m_2 + m_3)} \right]^{1/2}$$
(8.4)

From the conditions (8.4) it follows, for example, that with the masses being equal,  $m_1 = m_2 = m_3$ , the angle  $0 = 30^\circ$  and, hence, the angle between the axes is  $60^\circ$ . At the same time, the factor C, which specifies the extent of change of the scale of the rectangular coordinates for the transition to  $r_2$ , is equal to unity. The rectangular coordinates ( $\theta = 0$ ) are applicable when the ratios  $m_1/m_2$  or  $m_3/m_2$  are small (for example, for the reaction H +  $H(r_1) = H(r_2) + H(r_3) + H(r_4) + H(r_5) + H(r$ 

We are now in a position to represent the reaction  $X + YZ \rightarrow XY + Z$  under discussion by the travel of the particle  $m^*$  along

the reaction coordinate. To do this, let us return to the energy profile of the path, i.e., to Fig. 8.3 in which the particle  $m^*$  is shown by a filled circle. If this particle has initially a sufficient kinetic energy, it can ascend to the saddle point and then roll down with an ever increasing velocity into the exit valley. In other words, in this case, in our triatomic system the relative kinetic energy upon approach of the particles X + YZ is high enough for the repulsive forces to be overcome and for the transition state to be formed. The transition state complex is then decomposed and the reaction products fly apart with an ever increasing velocity.

From the above standpoint it must be understandable that the rate at which the given elementary reaction act proceeds is determined by the velocity with which the representative particle m\* moves across the top of the potential energy barrier. In different reaction acts the velocities will be quite different—this is in fact the manifestation of the thermal motion of molecules. At a given temperature, however, this velocity may be characterized by a certain mean value. We shall calculate it at a later time. Further, to simplify the calculation, it is useful to assume the existence of a flat portion on the reaction path, of length  $\delta$ , at the crest of the barrier. This is, in principle, tantamount to assuming that the transition state exists not at one point with the strictly fixed distances  $r'_1$  and  $r'_2$  but within a certain interval of these distances. The quantity  $\delta$  is here arbitrary and is introduced only for the sake of clarity into the calculations and is dropped out from the final result. Since the crest of the mountain pass is assumed to be flat, the motion of the representative particle on this portion of the reaction path may be regarded as one-dimensional and the average velocity with which the particle passes over the barrier can be calculated as the average velocity of thermal motion of molecules of mass  $m^*$  along one coordinate. This velocity is known from formula (6.8):

$$\overline{\dot{x}} = \left(\frac{kT}{2\pi m^*}\right)^{1/2}$$

Now, knowing the portion of the path on which there exists the transition state we can easily find its average lifetime:

$$\tau = \frac{\delta}{\bar{k}} = \delta / \left(\frac{kT}{2\pi m^*}\right)^{1/2} \tag{8.5}$$

The decomposition of the transition state, i.e., the reaction

$$X \cdots Y \cdots Z \longrightarrow X + YZ$$

is naturally thought to be unimolecular and first order. But for such reactions, as has been shown earlier (see Sec. 2.1), the av-

erage lifetime is the inverse of the reaction rate constant. Hence, the rate constant of the decomposition of  $X \cdots Y \cdots Z$  is determined by the relation

$$k_{\mathrm{I}}^{\neq} = \frac{1}{\tau} = \left(\frac{kT}{2\pi m^*}\right)^{1/2} \frac{1}{\delta} \tag{8.6}$$

and the observed reaction rate is equal to

$$\mathbf{w} = k_1^{\neq} c^{\neq} = \left(\frac{kT}{2\pi m^*}\right)^{1/2} \frac{1}{\delta} c^{\neq} \tag{8.7}$$

Here  $c^{\neq}$  is the concentration of activated complexes; it is unknown and must be replaced by more readily determinable quantities. This is done on the basis of the assumption (introduced by Arrhenius) of the equilibrium between the activated states and the reactants:

$$X + YZ \implies X \cdots Y \cdots Z$$

We may thus write the equilibrium constant

$$K_c^{\neq} = \frac{c^{\neq}}{c_{\mathbf{X}}c_{\mathbf{Y}Z}} \tag{8.8}$$

This relation can then be solved for the concentration  $c^{\neq}$  and the solution substituted into the equation for the reaction rate. We get

$$w = \left(\frac{kT}{2\pi m^*}\right)^{1/2} \frac{1}{\delta} K_c^{\neq} c_X c_{YZ} \tag{8.9}$$

Now we pass from the rate to the rate constant, taking advantage of the basic law expression for the initial bimolecular reaction:

$$w = k_{\rm H} c_{\rm X} c_{\rm YZ} \tag{8.10}$$

Comparing the last two expressions, we find the rate constant for the reaction under consideration:

$$k_{II} = \left(\frac{kT}{2\pi m^*}\right)^{1/2} \frac{1}{\delta} K_c^{\neq} \tag{8.11}$$

The rate constant of any other reaction will be expressed in exactly the same manner; the only difference will be in the method of writing the equilibrium constant for the activated complex,  $K_c^{\neq}$ , the determination of which will now be taken up.

It will be most expedient to make use of the methods of statistical thermodynamics discussed in Chapter 5; these methods allow the equilibrium constant to be expressed in terms of the partition functions per unit volume q [Eq. (5.63)]. For the given case, the equilibrium constant will have the following form:

$$K_c^{\neq} = \frac{(q^{\neq})}{q_{\mathcal{X}}q_{\mathcal{Y}\mathcal{Z}}} e^{-E_0^{\neq}/RT}$$
(8.12)

Here the numerator of the exponent must have contained the heat of the reaction at absolute zero but in the given case it is replaced by the energy consumed for the formation of the activated complex—the energy of activation at absolute zero,  $E_0^{\neq}$ . In the expanded form  $E_0^{\neq}$  is written as follows:

$$E_0^{\neq} = U_0^{\neq} - U_{0 \text{ (X)}} - U_{0 \text{ (YZ)}}$$

where  $U_{0(i)}$  are the zero-point energies of the participants of the activation process.

The partition functions of the reactants,  $q_x$  and  $q_{YZ}$ , are usually found without considerable difficulties on the basis of the molecular characteristics, for example, by the approximate methods described in Chapter 5. As regards the partition function of the activated complex  $(q^{\neq})$ , it is first decomposed into two cofactors, extracting from the total sum the term corresponding to the unidimensional translational motion of the representative particle  $m^*$  across the top of the energy barrier. Using the respective expression from Chapter 5, we get

$$(q^{\neq}) = q^{\neq} \frac{(2\pi m^* k T)^{1/2}}{h} \delta \tag{8.13}$$

where  $q^{\pm}$  is the partition function of the activated complex for all the other kinds of energy, i.e., the three degrees of freedom of translational motion in ordinary space and also the electronic, vibrational and rotational energies. Substituting the partition function  $(q^{\pm})$  from Eq. (8.13) into the equilibrium constant and the latter into the rate constant (8.11), we arrive at the expression

$$k_{\rm II} = \left(\frac{kT}{2\pi m^*}\right)^{1/2} \frac{1}{\delta} \cdot \frac{(2\pi m^* kT)^{1/2}}{h} \delta \frac{q^{\neq}}{q_{\rm X} q_{\rm YZ}} e^{-\frac{E_0^{\neq}}{kT}}$$

or

$$k_{\rm II} = \frac{kT}{h} \cdot \frac{q^{\neq}}{q_{\rm X}q_{\rm YZ}} e^{-\frac{E_0^{\neq}}{RT}}$$
(8.14)

which no longer contains the auxiliary quantities  $m^*$  and  $\delta$ . Equation (8.14) is the general expression for the rate constant of the reaction under consideration, which involves three atoms. It contains the universal factor kT/h, which has the dimensions of the frequency (sec)<sup>-1</sup>, a fraction including the partition functions, and an exponential function with the energy of activation. On the whole, as has been found, the pre-exponential factor does not depend strongly on temperature and can be compared with the corresponding factor of the Arrhenius equation. Hence, the

entire equation (8.14) is an equation of the Arrhenius equation type. It may also be noted that for any other reaction the expression for the rate constant has the same form—the only difference is in the method of writing the fraction with partition functions, which represents the equilibrium constant.

At this point it is expedient to consider the nature of the activated complex from a physical viewpoint. It may be regarded as a normal molecule, the only difference from a stable molecule being that it has one less vibrational degree of freedom and, instead, there appears translation along the reaction path; the latter

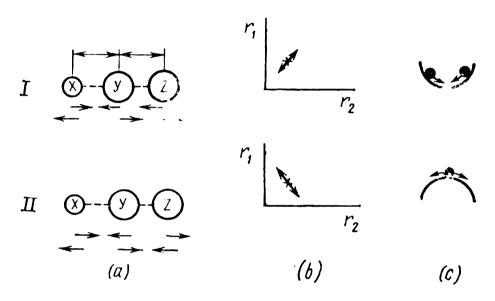


Fig. 8.5. The persistent (1) and disappearing (11) valence vibrations in a linear triatomic activated complex:

(a)—phases of vibrations; (b)—corresponding vibrations of the representative particle  $m^k$  along the potential-energy surface; the cross is the saddle point; (c)—energy profile of the reaction path.

refers to the reacting complex and may be disregarded when the complex is treated as a normal molecule. But what kind of vibrational motion is absent in the activated complex? The answer to this question is provided by Fig. 8.5. Two kinds of valence vibrations in a triatomic linear activated complex are shown. From Fig. 8.5 it must be clear that only the first vibration is stable, which is associated with the simultaneous decrease or increase of the internuclear distances  $r_1$  and  $r_2$ . In this case, the representative particle is situated in the potential well, which makes possible a periodic motion. In the second mode of vibration possible in the stable molecule, the representative particle is situated at the top of the energy hump (Fig. 8.5, c), from which it can descend in either direction. The deformation vibrations inherent in a linear triatomic molecule are stable in the activated complex as well.

The equation derived for the rate constant is usually supplemented by introducing the so-called transmission coefficient  $\varkappa$ , which takes account of the possibility of the representative particle  $m^*$ 

"rolling" also into the valley of the reactants, i.e.,

$$k_{II} = \varkappa \frac{kT}{h} \cdot \frac{q^{\neq}}{q_X q_{YZ}} e^{-E_0^{\neq}/RT}$$
(8.15)

The quantity  $\varkappa$  is apparently equal to or less than unity; there are no methods of calculating this quantity theoretically.

Let us, finally, write the rate constant in the most general form:

$$k = \varkappa \frac{kT}{h} \left( K_c^{\neq} \right) \tag{8.16}$$

Here the following notation is introduced:

$$\left(K_{c}^{\neq}\right) = \frac{a^{\neq}}{q_{X}q_{YZ}} e^{-E_{0}^{\neq}/RI}$$

The quantity  $(K_c^{\neq})$  may be regarded as the equilibrium constant with respect to the activated complex as a normal molecule;  $(K_c^{\neq})$  is evidently different from the previously introduced constant  $K_c^{\neq}$  which refers to the activated complex moving along the reaction path. \*

### 8.3. Application of the Basic Law to Individual Types of Reactions

Recombination of two atoms and comparison with the collision theory. Interesting results are obtained if the basic equation (8.15) is applied to a bimolecular reaction involving two atoms:

$$X + Y \longrightarrow X \cdots Y \longrightarrow XY$$

Equation (8.15) assumes the following form in this case

$$k_{II} = \varkappa \frac{q^{\neq}}{q_{\chi}q_{\chi}} e^{-E_0^{\neq}/RI}$$
 (8.17)

The diatomic activated complex has three translational degrees of freedom and two rotational degrees of freedom. Vibrational motion is absent. In accordance with the approximate formulas of Chapter 5, its partition function may be written thus

$$q^{\neq} = g^{\neq} \frac{\left[2\pi \left(m_{X} + m_{Y}\right) kT\right]^{3/2}}{h^{3}} \cdot \frac{8\pi^{2} I^{\neq} kT}{h^{2}}$$
$$I^{\neq} = D_{X...Y}^{2} \frac{m_{X} m_{Y}}{m_{X} + m_{Y}} = D_{X...Y}^{2} \mu$$

<sup>\*</sup> The partition function of the activated complex  $(q^{\neq})$  contained a term for this motion.

in which  $g_0^{\neq}$  is the degeneracy of the ground electronic level;  $m_X$  and  $m_Y$  are the actual masses of the atoms; and  $I^{\neq}$  is the moment of inertia of the activated complex.

The partition functions of the starting atoms are represented only by the electronic factors and the components of translational motion:

$$q_{\rm X} = g_{0({\rm X})} \frac{\left(2\pi m_{\rm X} kT\right)^{3/2}}{h^3}$$
 and  $q_{\rm Y} = g_{0({\rm Y})} \frac{\left(2\pi m_{\rm Y} kT\right)^{3/2}}{h^3}$ 

Substituting the partition function into Eq. (8.17), we get

$$k_{II} = \varkappa \frac{g_0^{\neq}}{g_{0(X)}g_{0(Y)}} D_{X...Y}^2 \left\{ 8\pi kT \left( \frac{1}{m_X} + \frac{1}{m_Y} \right) \right\}^{1/2} e^{-E_0^{\neq}/RT}$$
 (8.18)

The resulting equation can be simplified if we ignore the factor  $g_0^{\neq}/g_{0(X)}g_{0(Y)}$ , which cannot be much different from unity since the degeneracies of ground electronic levels are equal either to unity or to small integers. Setting tentatively the transmission coefficient equal to unity and introducing the molecular weights, we write

$$k_{11} = D_{X...Y}^{2} \left\{ 8\pi RT \left( \frac{1}{M_{X}} + \frac{1}{M_{Y}} \right) \right\}^{1/2} e^{-E_{0}^{\neq}/RT}$$
 (8.19)

This expression practically coincides with the formula of simple collision theory (7.11) and, hence, both theories lead in this case to identical results.

Certain differences can be noted between  $D_{\text{X} \dots \text{Y}}$  and  $D_{\text{AB}}$  and also between  $E_0^{\neq}$  and E. As is clear from the foregoing,  $D_{\text{X} \dots \text{Y}}$  is the internuclear distance in the activated complex, and  $D_{\text{AB}}$  is the average gas-kinetic collision diameter. Of these quantities  $D_{\text{X} \dots \text{Y}}$  has a clearer physical meaning and preference should be given to this quantity. On the other hand, the energy of activation  $E_0^{\neq}$  refers to absolute zero and not to the reaction temperature. This difference is more serious but has no practical importance because of the low accuracy of calculation of  $E_0^{\neq}$  even in those cases when it is generally possible. In any event, on the basis of Eqs. (8.19) and (7.10) we can put

$$Z_0 = D_{X \dots Y}^2 \left\{ 8\pi RT \left( \frac{1}{M_Y} + \frac{1}{M_Y} \right) \right\}^{1/2} \approx A$$
 (8.20)

where  $Z_0$  is the frequency factor of the collision theory and A is the pre-exponential factor in the Arrhenius equation. The coincidence of the basic relations is undoubtedly of fundamental importance since it points to the well-known similarity between the two theories or, more exactly, indicates that the more general sta-

tistical transition-state theory incorporates simple collision theory as an element. The coincidence has no practical importance in this case since the full expression for the rate constant includes a transmission coefficient which is of the order of  $10^{-14}$  for a reaction of two atoms, i.e., no bimolecular recombination of atoms occurs.

It is more expedient to make use of the resulting relation for a further comparison of transition-state theory and collision theory. To simplify the problem, we shall assume that the partition function for each kind of energy may be expressed by the product of a certain number of identical factors—one for each degree of freedom. Thus, denoting through  $Q_{\rm tr}$ ,  $Q_{\rm rot}$ , and  $Q_{\rm vib}$  the partition functions of the translational, rotational and vibrational degrees of freedom, we write for the general case:

$$q = Q_{ij}^t Q_{rot}^r Q_{vib}^v \tag{8.21}$$

where t, r, and v are the numbers of the corresponding degrees of freedom. For the above-considered reaction between two atoms

$$q_{\rm X} = Q_{\rm tr}^3$$
,  $q_{\rm Y} = Q_{\rm tr}^3$  and  $q^{\neq} = Q_{\rm tr}^3 Q_{\rm res}^2$ 

Hence,

$$Z_0 = \frac{kT}{h} \cdot \frac{q^{\neq}}{q_X q_Y} \approx \frac{kT}{h} \cdot \frac{Q_{\text{rot}}^2}{Q_{\text{tr}}^3}$$
 (3.22)

and the quantity (kT/h)  $Q_{\rm rot}^2/Q_{\rm tr}^3$  may be considered to be equal to the collision frequency at unit concentrations  $(n_{\rm X}=n_{\rm Y}=1)$ , which is what follows from formula (8.20).

If we pass from two atoms to a bimolecular reaction between two non-linear molecules A and B with the number of atoms  $n_A$  and  $n_B$  then

$$q_{\rm A} = Q_{\rm tr}^3 Q_{\rm rot}^3 Q_{\rm vib}^{3n_{\rm A}-6}$$
$$q_{\rm B} = Q_{\rm tr}^3 Q_{\rm rot}^3 Q_{\rm vib}^{3n_{\rm B}-6}$$

and

$$q^{\neq} = Q_{\text{tr}}^{3} Q_{\text{rot}}^{3} Q_{\text{vib}}^{3(n_{\text{A}} + n_{\text{B}}) - 7}$$

since the activated complex has one less vibrational degree of freedom than a normal molecule consisting of  $n_A + n_B$  atoms. We denote the pre-exponential factor of the equation for the reaction under consideration as A. Then

$$A = \frac{kT}{h} \cdot \frac{q^{\neq}}{q_{A}q_{B}} \approx \frac{kT}{h} \cdot \frac{Q_{\text{vib}}^{5}}{Q_{\text{tr}}^{3}Q_{\text{rot}}^{3}}$$

or, on the basis of Eq. (8.22),

$$A \approx Z_0 \left(\frac{Q_{\text{vib}}}{Q_{\text{rot}}}\right)^5 \tag{3.23}$$

Thus, the frequency factor of the statistical theory will differ in this most general case of a bimolecular reaction from the quantity  $Z_0$  of simple collision theory by  $(Q_{\rm vib}/Q_{\rm rot})^5$  times. As known,  $Z_0$  does not correspond in many cases to the experimental pre-exponential factor in the Arrhenius equation; to bring them into agreement, the steric factor smaller than unity is introduced. Since the ratio  $Q_{\rm vib}/Q_{\rm rot}$  is also smaller than unity, it has been suggested that

$$P \approx \left(\frac{Q_{\text{vib}}}{Q_{\text{rot}}}\right)^5$$

This refers to the interaction between non-linear molecules. Analogous calculations for molecules of other types can be given (Table 8.1).

TABLE 8.1. Expressions for the Steric Factor in a Bimolecular Reaction Involving Different Types of Molecules

Types of reacting molecules	P	
Two atoms	1	
An atom and a diatomic molecule		
a non-linear complex	$Q_{\rm vib}/Q_{\rm rot}$	
a linear complex	$(Q_{\text{vib}}/Q_{\text{rot}})^2$	
An atom and a polyatomic molecule	$(Q_{\text{vib}}/Q_{\text{rot}})^2$	
Two diatomic molecules		
a non-linear complex	$(Q_{\text{vib}}/Q_{\text{rot}})^3$	
a linear complex	$(Q_{\text{vib}}/Q_{\text{rot}})^4$	
A diatomic and a polyatomic molecule	$(Q_{\rm vib}/Q_{\rm rot})^4$	
Two polyatomic molecules	$(Q_{\text{vib}}/Q_{\text{rot}})^5$	

In connection with the data presented in Table 8.1 it may be pointed out that, as a rule, the vibrational partition function is lower than the rotational partition function by one or two orders of magnitude;  $Q_{\rm vib}$  is close to unity for not too weak vibrations and ordinary temperatures and  $Q_{\rm rot}$  usually has values from 10 to 100. Therefore, the ratio  $Q_{\rm vib}/Q_{\rm rot}$  may be found to range from  $10^{-1}$  to  $10^{-2}$  and the power of this ratio, which determines the

steric factor P according to the theory, will decrease with increasing complexity of reacting molecules. Such is the plausible qualitative interpretation of the steric factor within the framework of the statistical theory.

A somewhat different approach to the determination of P will be given at a later time in connection with the thermodynamic aspect of the theory.

Formation of Hydrogen Iodide. The bimolecular reaction

$$H_2 + I_2 = 2HI$$

proceeds most probably via the formation of a planar symmetrical complex of the type shown in Fig. 8.6. Based on the participation

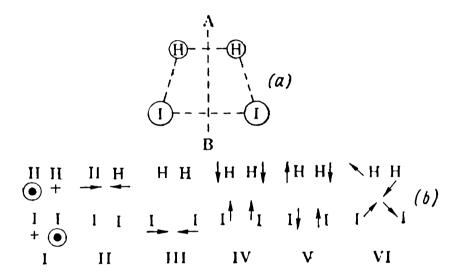


Fig. 8.6. Concerning the reaction of formation of hydrogen iodide: (a)—expected configuration of the activated complex  $H_2I_2$ , which is symmetrical with respect to the plane AB; (b) — modes of vibration of the atoms in the complex:

I—deformation vibrations; II—vibrations leading to decomposition.

in the reaction of one electron from each of the atoms, we can solve a quantum-mechanical problem called the four-electron problem. Without going into the details, we only point out that the solution of the corresponding secular equation may, in principle, lead to the configuration of atoms with an energy which is maximal in the direction of the reaction path and minimal with respect to all other deformations. The solution of the problem is considerably facilitated by the use of mechanical devices, for example, six hinged or sliding rulers (suggested by Altar and Eyring) on each of which are marked the values of one of the six binding energies as a function of the internuclear distances. The data required for drawing up these scales are obtained in a general case, if all the four atoms are different, from the six Morse functions for six diatomic molecules. It is understandable that for H<sub>2</sub>I<sub>2</sub> the number of required functions is reduced. In the four-atom complex H<sub>2</sub>I<sub>2</sub> there are 6 normal vibrations shown in Fig. 8.6;

the frequencies of these vibrations can also be calculated, though less accurately.

Below are given some of the calculated results (in cm<sup>-1</sup>);

$$v_{\rm I}$$
  $v_{\rm II}$   $v_{\rm III}$   $v_{\rm IV}$   $v_{\rm V}$   $v_{\rm VI}$  994 86 1280 965 1400 1730

In view of the configuration of  $H_2I_2$  being symmetrical with respect to the AB plane it is sufficient to know three interatomic distances. Calculations have given the following results:  $r_{(H-H)} = 0.97$ ,  $r_{(H-I)} = 1.75$ ,  $r_{(I-I)} = 2.95$  Å. The three inertial moments of the activated complex take on the following values:

$$I_a$$
  $I_b$   $I_c$  921.5 6.9 928.5 g·cm<sup>2</sup>·10<sup>40</sup>

The moments of inertia for the molecules  $H_2$  and  $I_2$  are respectively equal to 0.456 and  $748.5 \times 10^{-40}$  g·cm<sup>2</sup>. The energy of activation  $(E_0)$  calculated to a low accuracy  $(E_0 = 49.6 \text{ kcal})$  is found to be by almost 25 per cent higher than that determined on the basis of experimental data ( $E_0 = 40 \text{ kcal}$ ). For the reaction between iodine and hydrogen the equation for

the rate constant of reaction, (8.15), becomes

$$k_{II} = \varkappa \frac{kT}{h} \cdot \frac{\frac{(2\pi m^{\frac{1}{2}}kT)^{\frac{3}{2}}}{h^{3}}}{\frac{(2\pi m_{1}kT)^{\frac{3}{2}}}{h^{3}} \cdot \frac{(2\pi m_{2}kT)^{\frac{3}{2}}}{h^{3}}}{\frac{8\pi^{2} (8\pi^{3}I_{a}I_{b}I_{c})^{\frac{1}{2}} (kT)^{\frac{3}{2}}}{\sigma^{\frac{1}{2}}h^{3}}} \times \frac{\frac{8\pi^{2}I_{1}kT}{\sigma^{\frac{1}{2}}} \cdot \frac{8\pi^{2}I_{2}kT}{\sigma^{\frac{1}{2}}h^{2}}}{\frac{8\pi^{2}I_{1}kT}{\sigma^{\frac{1}{2}}h^{2}}}}{\frac{1}{(1-e^{-h\nu^{\frac{1}{2}}/kT})^{-1}}}e^{-E_{0}^{\frac{1}{2}}/RT}$$

$$\times \frac{\prod_{j=1}^{5} (1-e^{-h\nu^{\frac{1}{2}}/kT})^{-1}}{(1-e^{-h\nu^{\frac{1}{2}}/kT})^{-1}}e^{-E_{0}^{\frac{1}{2}}/RT}$$

$$(8.24)$$

Here, an approximate method is used (see Chapter 5) to interpret the partition functions  $q_i$ , which is based on the assumption of the independency of the individual types of motion. The numerator refers to the activated complex and the denominator to the reactants.

The symmetry number  $\sigma^{\neq}$  is equal to 4 and  $\sigma_1$  and  $\sigma_2$  are equal to 2, so that in Eq. (8.24) they cancel out. The electronic and nuclear factors are assumed to be equal to unity.

With all these data no values of the constants being in satisfactory agreement with experimental values are obtained. But if certain corrections are introduced into the explicitly inaccurate frequencies, namely, if  $v_5$  and  $v_6$  are assumed to be equal to 180 and 1000 cm<sup>-1</sup>, a certain agreement can be arrived at. If further we assume  $\log k = 1.808$  at 700 K as the initial experimental value, then, first, the energy of activation,  $E_0$ , will be equal to 39.7 kcal. Second, the constants calculated with such corrections introduced for other temperatures agree satisfactorily with experimental values (Table 8.2).

<i>Т</i> . К	$\log k_{11}$		
	obtained experimentally	calculated	
575	-0.88	-0.85	
700	1.808	1.808	
781	3.13	3.09	

TABLE 8.2. Calculated and Experimental Rate Constants for the Reaction of Hydrogen Iodide

Of course, these agreements may be recognized as a certain achievement of the theory, but a complete theoretical calculation of the reaction rate, which is exactly what is claimed by the theory of absolute reaction rates, still remains, strictly speaking, to be a mere possibility.

### 8.4. The Thermodynamic Aspect of Transition-State Theory

Neglecting the transmission coefficient, let us define the rate constant of a reaction in the following general form:

$$k_{r} = \frac{kT}{h} \left( K^{\neq} \right) \tag{8.25}$$

Here  $(K^{\neq})$  is the equilibrium constant for the process of formation of an activated complex which is regarded as a normal molecule. The equilibrium constant can be expressed with the aid of the well-known thermodynamic equation

$$RT \ln (K^{\neq}) = -\Delta G^{\neq} \tag{8.26}$$

where  $\Delta G^{\neq}$  is the standard \* free energy of activation. Using

<sup>\*</sup> The notation usually adopted for the standard free-energy change is  $\Delta G^0$ . Though the zero superscript is omitted here, it must be remembered that all the changes of the thermodynamic functions are used on the assumption that both the reactants and the activated complex are in their standard states. Thus, Eq. (8.26) relating  $K_c$  to  $\Delta G^0$  is valid only under standard conditions with molar concentrations (say, mole/ml) being equal to unity and not with the pressures  $p_i^0 = 1$  atm. In thermodynamics, the letter G is used to denote the Gibbs free energy.

this expression, we may introduce the free energy into the expression (8.25) for the rate constant:

$$k_r = \frac{kT}{h} e^{-\Delta G \neq /RT} \tag{8.27}$$

At constant temperature  $\Delta G^{\neq}$  is expressed in terms of standard changes of enthalpy and entropy:

$$\Delta G^{\neq} = \Delta H^{\neq} - T \Delta S^{\neq}$$

Therefore, Eq. (8.27) may be rewritten also in the following form:

$$k_r = \frac{kT}{h} e^{\Delta S \neq /R} e^{-\Delta H \neq /RT}$$
(8.28)

where  $\Delta H^{\neq}$  and  $\Delta S^{\neq}$  are, respectively, the standard heat at constant pressure and the standard entropy of the formation of an activated complex.

Equations (8.27) and (8.28) show that, strictly speaking, it is the free energy of activation that determines the reaction rate and not simply the energy or heat of the process, as it follows from the Arrhenius concepts. True, only in those not rare cases when the change in entropy accompanying the activation process is insignificant, is the effect of the activation heat predominating.

To compare Eq. (8.28) with experimental data and to deduce certain consequencies, we must dispense with the directly indeterminable activation enthalpy and replace it with the experimental energy of activation,  $E_A$ . For this replacement to be correct, it is necessary to carry out a certain procedure. If the rate constant is expressed in terms of concentration units, the standard state may also be conveniently defined as one with a concentration of 1 mole/cm<sup>3</sup>. Having agreed on this, we take logarithms of Eq. (8.25):

$$\ln k_r = \ln \frac{k}{h} + \ln T + \ln \left( K_c^{\neq} \right)$$

Differentiating this relation with respect to temperature and using also the Arrhenius equation and the van't Hoff equation, we obtain

$$\frac{d \ln k_r}{dT} = \frac{E_A}{RT^2} = \frac{1}{T} + \frac{d \ln \left(K_c^{\neq}\right)}{dT} = \frac{1}{T} + \frac{\Delta U^{\neq}}{RT^2}$$

Hence

$$E_{\mathbf{A}} = RT + \Delta U^{\neq} = RT + \Delta H^{\neq} - \rho \, \Delta V^{\neq} \tag{8.29}$$

Here  $\Delta U^{\neq}$  is the change in internal energy of the system during the activation process; if the system is ideal, then  $\Delta U^{\neq}$  as well as  $\Delta H^{\neq}$  is independent of the selection of the standard state. But

for  $\Delta S^{\neq}$  the nature of the standard state becomes essential. Therefore, we rewrite Eq. (8.28) in the following form:

$$k_r = \frac{kT}{h} e^{\Delta S_c^{\neq}/R} e^{-\Delta H^{\neq}/RT}$$

and substitute  $\Delta H^{\neq}$  from Eq. (8.29) into this expression. We get:

$$k_r = \frac{kT}{h} e^{\Delta S_c^{\neq}/R} e^{-(E_A - RT + \rho \Delta V^{\neq})/RT}$$

For a gas reaction,  $p\Delta V^{\neq}$  is approximately equal to  $\Delta n^{\neq}RT$ , where  $\Delta n^{\neq}$  is the change in the number of molecules during the formation of an activated complex. Therefore,

$$k_r = \frac{kT}{h} e^{-(\Delta n \neq -1)} e^{\Delta S_c^{\neq}/R} e^{-E_A/RT}$$

If the reaction involves x molecules and leads to the formation of a single transition-state molecule, then  $\Delta n^{\neq} = 1 - x$  and, hence,

$$k_r = \frac{kT}{h} e^x e^{\Delta S_c^{\neq}/R} e^{-E_A/RT}$$
(8.30)

In thermodynamics, another standard state is usually employed, namely, that of an ideal gas at 1 atm pressure. All the tabulated values of entropy are referred to this system of standardization. Therefore, it is expedient to make use of the following thermodynamic relationship \*

$$\Delta S_c = \Delta S_p - \Delta nR \ln RT = \Delta S_p - (1 - x) R \ln RT$$

where  $\Delta S_p$  is the change in entropy during the activation process when both the reactants and the transition state complex are at a pressure of 1 atm.

With  $\Delta S_p$  the equation assumes the following form

$$\dot{R}_{r} = \frac{kT}{h} e^{x} e^{-(1-x)\ln RT} e^{\Delta S_{p}^{\neq}/R} e^{-E_{A}/RT} = \frac{kT}{h} e^{x} (RT)^{x-1} e^{\Delta S_{p}^{\neq}/R} e^{-E_{A}/RT}$$
(8.31)

For a bimolecular reaction, x=2 and therefore Eqs. (8.30) and (8.31), with the transmission coefficient being taken into account,

\* Here use is made of the well-known thermodynamic formula for the isothermal change of the entropy of an ideal gas:  $S_2 - S_1 = R \ln \frac{P_1}{P_2}$ . If  $P_2 = 1$  atm, then  $S_2 = S_p^\circ$  (standard entropy at P = 1 atm). If  $P_1 = RT/V_1$ , where  $V_1 = 1$  cm³/mole, then  $S_1 = S_c^\circ$  (the standard entropy at a concentration of c = 1 mole/cm³). Consequently,  $S_p^\circ = S_c^\circ + R \ln RT$ . In connection with the last formula, it must be noted that if R outside the logarithm is expressed in the same units as the entropy (usually, in cal·deg<sup>-1</sup>·mole<sup>-1</sup>), then for the expression for R under the logarithm we must put 82.06 cm³·atm·deg<sup>-1</sup>·mole<sup>-1</sup>.

will become

$$k_r = \kappa e^2 \frac{kT}{h} e^{\Delta S_c^{\neq}/R} e^{-E_A/RT}$$
(8.32)

and

$$k_r = \kappa e^2 \frac{kT}{h} RT e^{\Delta S_p^{\neq}/R} e^{-E_A/RT}$$
(8.33)

For a molecular reaction, x = 1 and, hence,

$$k_r = \varkappa e \frac{kT}{h} e^{\Delta S \neq /R} e^{-E_A/RT}$$
(8.34)

In this last case the entropy of activation is independent of the choice of the standard state and the numerical values of the rate constant depend on the concentration units.

It is interesting to establish further at what values of the entropy of activation the simple collision theory will give correct results or, in other words, what entropy of activation will correspond to a "normal" bimolecular reaction (Chapter 7, Sec. 7.1), for which the frequency factor  $Z_0 = 2.8 \times 10^{14}$  cm<sup>3</sup>/mole·sec, (Eq. 7.16). We shall now calculate the factor before the entropy term of Eq. (8.32) without the indeterminable coefficient  $\varkappa$  for "ordinary" temperatures, say, 600 K:

$$\frac{kT}{h}e = \frac{1.38 \times 10^{-16} \times 600}{6.7 \times 10^{-27}} (2.7)^2 \approx 10^{14}$$

Thus, for "normal" reactions of the simple collision theory the entropy term itself,  $e^{\Delta S_c^{\neq}/RT}$ , must be approximately equal to  $2.8 \approx e$ . In other words, the entropy of activation  $\Delta S_c^{\neq}$  is equal in this case to R, i.e.,  $2 \text{ cal/deg \cdot mole}$ , and is a small positive value. On the basis of this calculation we can assume that if the entropy of activation is close to zero, i.e.,  $\Delta S_c^{\neq} = 0$ , then the numerical value of the pre-exponential factor of Eq. (8.32) corresponds to the normal reaction, i.e.,  $Z_0 = 2.8 \times 10^{14} \text{ cm}^3/\text{mole \cdot sec}$ .

But if  $\Delta S_c^{\neq} \gg 0$ , then the entropy term

$$e^{\Delta S_c^{\neq}/RT} \gg 1$$

and the pre-exponential factor will be greater than the normal value: this is a case of "fast" reactions. On the contrary, if  $\Delta S_c^{\neq} \ll 0$ , the entropy term

$$c^{\Delta S_c^{\neq}/RT} \ll 1 \tag{8.35}$$

and the pre-exponential factor will be smaller than the normal value and will evidently correspond to "slow" reactions.

Hence, the change of the entropy during the formation of an activated complex directly determines the numerical value of the pre-exponential factor in an equation of the Arrhenius equation type and is formally one of the quantities that determine the rate of the reaction. Since the quantity  $e^2kT/h$  coincides, in order of magnitude, with the normal quantity  $Z_0$  of the collision theory, then the entropy term  $\exp\left(\Delta S_c^{\neq}/R\right)$  acquires the meaning of the steric or probability factor P formally introduced by the theory of activated collisions.

### 8.5. Unimolecular Reactions

Certain advances have been achieved by the transition-state theory in calculating the frequency factors for unimolecular reactions:

$$A \longrightarrow A^{\neq} \longrightarrow B + C$$

In this case the basic equation of the type (8.15) takes the form

$$k_{\rm I} = \varkappa \, \frac{kT}{h} \cdot \frac{q^{\neq}}{q_{\rm A}} \, e^{-E_0^{\neq}/RT} \tag{8.36}$$

The activated complex  $A^{\neq}$ , which is probably formed by way of a fruitful activating collision, is a molecule consisting of the same number of atoms and evidently does not strongly differ in structure from the original molecule, only one or more of its bonds are in the process of being broken. This difference will be manifested in the disappearance of one vibrational degree of freedom. In view of what has been said, it is reasonable to assume, as is ordinarily done in discussing the steric factor of bimolecular reactions, that the partition functions are equal to the product of a series of cofactors which are the same for all the degrees of freedom of a given type of motion. Then Eq. (8.36) will be rewritten in the form

$$k_{1} = \varkappa \frac{kT}{h} \cdot \frac{\left(Q_{\text{tr}}^{3} Q_{\text{rot}}^{3} Q_{\text{vib}}^{3n-7}\right)^{\neq}}{Q_{\text{tr}}^{3} Q_{\text{rot}}^{3} Q_{\text{vib}}^{3n-6}} e^{-E_{0}^{\neq}/RT}$$
(8.37)

Here the reactant molecule and the activated complex are considered to be n-atomic non-linear molecules.

The translational partition functions, which depend only on temperature and the total mass of the molecule, are evidently the same in the initial and transition states. In the rotational partition functions all the constant quantities will cancel out and there will remain only the symmetry numbers and moments of inertia if it is assumed that they are different in the activated complex and in the reactant molecule. In a non-linear reactant molecule there are 3n-6 modes of vibration, and in the activated com-

plex there is one less vibrational degree of freedom (3n-7). As a result of this detailing, Eq. (8.37) becomes

$$k_{1} = \varkappa \frac{\sigma_{i}}{\sigma^{\neq}} \cdot \frac{\left(I_{A}^{\neq} I_{B}^{\neq} I_{C}^{\neq}\right)^{1/2}}{\left(I_{A} I_{B} I_{C}\right)^{1/2}} \cdot \frac{\prod_{3n-6}^{3n-7} \left(1 - e^{-h\nu \neq /kT}\right)^{-1}}{\prod_{n=6}^{3n-6} \left(1 - e^{-h\nu i/kT}\right)^{-1}} \frac{kT}{h} e^{-\frac{E_{0}^{\neq}}{RT}}$$
(8.38)

Unfortunately, the equation in this more or less complete form is difficult to compare with experimental data: hypotheses are required concerning the detailed structure of the activated complex and the forces operating inside it and more or less unreliable estimations of the transmission coefficient  $\varkappa$  are unavoidable. Instead of all this, it is possible, by way of a further approximation, to consider the structure and other properties of the transition complex to be only slightly different from the respective data for the reactant molecule. In particular, the frequencies of all the vibrations are assumed to be identical, except for one which is replaced in the activated complex by the translation along the reaction coordinate. Then, Eqs. (8.37) and (8.38) simplify considerably:

$$k_1 = \frac{kT}{h} \cdot \frac{1}{Q_{\text{vib}}} e^{-E_0^{\neq}/RT} = \frac{kT}{h} (1 - e^{-h\nu/kT}) e^{-E_0^{\neq}/RT}$$
 (8.39)

Thus, first, the frequency factor of a unimolecular reaction is approximately equal to  $kT/hQ_{\rm vib}$ . At the same time, the simple collision theory leads [Eq. (8.22)] to the frequency factor  $(kT/h)Q_{\rm rot}^2/Q_{\rm tr}^3$  which is lower than that written above by  $Q_{\rm tr}^3/Q_{\rm rot}^2Q_{\rm vib}$  times. Since  $Q_{\rm tr}$  is relatively high, the frequency factor of the collision theory is found to be too small. Second, introducing a further approximation, we may take into account that for ordinary vibration frequencies and moderate temperatures the exponent hv/kT has a value of the order of several units. Therefore, the power in parentheses may be neglected as compared with unity and we may write a general approximate expression for the rate constant of unimolecular reactions in the following form:

$$k_{\rm I} = \frac{kT}{h} e^{-E_0^{\neq}/RT} \tag{8.40}$$

At a temperature of 300 K,  $kT/h = 0.6 \times 10^{13} \, \mathrm{sec^{-1}}$  and it thus follows that the frequency factor of Eq. (8.40) coincides in order of magnitude with the "normal" value obtained on the basis of experimental data (Table 7.2). Hence, the transition-state theory in a first approximation solves in quite a simple way the problem of unimolecular reactions.

Equation (8.40) is derived on the assumption that  $hv \gg kT$ . But if, on the contrary, hv/kT is small, say, at high temperatures.

then, expanding the term  $\exp(-x) = \exp(-hv/kT)$  as a power series in x and rejecting all the terms after the second, we can obtain the following expression:

$$k_{\rm I} = ve^{-E_0^{\neq}/RT} \tag{8.41}$$

Here, according to the meaning of the derivation, v is the frequency of the vibration which is present in the reactant molecule and absent in the activated complex and which may be believed to occur along the bond being broken. The vibration frequencies usually range from  $10^{13}$  to  $10^{14}$  sec<sup>-1</sup>, so that, from this standpoint too, the theoretical pre-exponential factor of a unimolecular reaction corresponds to the "normal" value. The factor  $\exp(-E_0^{\neq}/RT)$  may be regarded as a fraction of micro-objects, whose energy in two quadratic terms is equal to or greater than  $E_0^{\neq}$ . Therefore, expression (8.41) gives a fraction of harmonic oscillators having an energy equal to or greater than  $E_0^{\neq}$  and therefore capable of entering into reaction. As can be easily seen, Eq. (8.41) coincides in form and is close in essence to Eq. (7.52) of the Slater theory, where v expresses the weighted mean frequency of oscillators.

Thus, the activated-complex theory has made certain advances also in the computation of the pre-exponential factors for unimolecular reactions.

#### 8.6. Termolecular Reactions

Table 7.6 gave a number of examples of third-order reactions. Of those listed only three reactions are ordinary chemical reactions (the interactions of nitric oxide with oxygen or halogens). It is for these reactions that the use of the collision theory has proved quite unsatisfactory and for the calculated reaction rate to be brought into agreement with the experimental value a steric factor of the order of  $10^{-6}$  to  $10^{-7}$  had to be introduced. Recombination processes in which a ternary collision is required for the removal of the excess energy from the newly formed melecule have been found to be in better agreement with the collision theory.

As has been established, the activated-complex theory leads to more satisfactory results also for reactions involving nitric oxide. We shall consider here the application of the theory of the activated complex (transition-state theory) exactly to these reactions which may be written in a general form:

$$2NO + X_2 = 2NOX$$

where X is oxygen or halogen.

The equation for the rate constant is written in a general form as follows:

$$k_{\text{III}} = \varkappa \frac{kT}{h} \cdot \frac{q^{\neq}}{q_{\text{NO}}^2 q_{X_2}} e^{-E_0^{\neq}/RT}$$
(8.42)

and when the partition functions are detailed, it becomes

$$k_{III} = \varkappa \frac{kT}{h} \cdot \frac{g^{\neq}}{\prod_{3}^{3} g_{i}} \cdot \frac{\frac{(2\pi m^{\neq} kT)^{3/2}}{h^{3}}}{\prod_{3}^{3} \frac{(2\pi m_{i} kT)^{3/2}}{h^{3}}} \times \frac{\frac{\pi^{1/2}}{\sigma^{\neq}} \left(\frac{8\pi^{2}kT}{h^{2}}\right)^{3/2} (I_{A}I_{B}I_{C})^{1/2}}{\prod_{3}^{3} \left(1 - e^{-h\nu_{i}/kT}\right)^{-1}} e^{-E_{0}^{\neq}/RT} \times \frac{\prod_{3}^{3} \frac{8\pi^{2}I_{i}kT}{\sigma_{i}h^{2}}}{\prod_{3}^{3} \left(1 - e^{-h\nu_{i}/kT}\right)^{-1}} e^{-E_{0}^{\neq}/RT}$$
(8.43)

Here, as before,  $\varkappa$  is the transmission coefficient which is then set to unity;  $g^{\#}$  and  $g_i$  are the degeneracies of the electronic levels in the activated complex and reactant molecules, respectively, and  $\sigma^{\#}$  and  $\sigma_i$  are the corresponding symmetry numbers. In a general case, the activated complex has three moments of inertia, the product of which,  $I_AI_BI_C$ , is included in the partition function of the total rotation of the complex. The complex consists of six atoms and must have 12-1=11 modes of vibration if no internal rotation takes place. Glasstone, Laidler, and Eyring suggest that all the temperature-dependent factors be picked out in Eq. (8.43) and those left be designated as G. The result is as follows:

$$k_{111} = G \frac{1}{T^{7/2}} \cdot \frac{\prod_{i=1}^{11} \left(1 - e^{-hv^{\neq}/kT}\right)^{-1}}{\prod_{i=1}^{3} \left(1 - e^{-hv_{i}/kT}\right)^{-1}} e^{-E_{0}^{\neq}/RT}$$
(8.44)

or

$$k_{111}T^{7/2} \frac{\prod_{i=1}^{3} \left(1 - e^{-hv_i/kT}\right)^{-1}}{\prod_{i=1}^{1} \left(1 - e^{-hv \neq /kT}\right)^{-1}} = Ge^{-E_0^{\neq}/kT}$$
(8.45)

Taking logarithms in the last expression and then differentiating with respect to the inverse temperature, we obtain

$$\frac{d}{d(1/T)} \ln \left\{ k_{111} T^{7/2} \frac{\prod_{i=1}^{3} \left(1 - e^{-h\nu_i/kT}\right)^{-1}}{\prod_{i=1}^{11} \left(1 - e^{-h\nu \neq /kT}\right)^{-1}} \right\} = -\frac{E_0^{\neq}}{R}$$
(8.46)

Hence, the ratio  $-(E_0^{\neq}/R)$  must represent the slope of the dependence of the logarithm of the expression in braces on the inverse temperature, 1/T. Thus, if we construct a plot of the quantity

$$\ln k_{III} + \frac{7}{2} \ln T + \ln \prod_{i=1}^{3} \left(1 - e^{-h\nu_i/kT}\right)^{-1} - \ln \prod_{i=1}^{11} \left(1 - e^{-h\nu \neq /kT}\right)^{-1}$$
 (8.47)

against the inverse temperature, then the slope of the resulting straight line must be equal to  $-E_0/R$ . Hence,  $E_0^{\neq}$  can be found

in this way with the rate constant being determined experimentally at several temperatures.

Equation (8.44) also permits the following approximate consideration. As has already been said in the preceding section, in connection with the theory of unimolecular reactions, at moderate temperatures the power of  $\exp(-hv/kT)$  is usually close to zero and, consequently, the entire fraction containing the vibrational partition functions may be equated to unity. Then we have

$$k_{111} = \frac{G}{T^{1/2}} e^{-E_{11}^{\neq}/RT}$$
 (8.48)

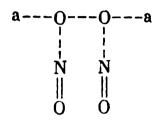


Fig. 8.7 The postulated model of the activated complex for the oxidation of nitric oxide

a---a is the axis of internal rotation.

and the pre-exponential factor is found to be strongly dependent on temperature ( $\propto T^{-3.5}$ ). Therefore, if  $E_0^{\neq}$  is equal to zero or is small, then the rate constant will diminish with increasing temperature as shown for the oxidation of nitric oxide (see Sec. 2.3). At not too small values of  $E_0^{\neq}$ , the rate constant  $k_{\rm HI}$  must increase at low temperatures and diminish at high temperatures. It is however difficult to say whether this is the case in reality since no sufficiently exact relationship has so far been established between the rate of termolecular reactions and temperature (see Table 7.6).

In a more detailed treatment of the kinetics of any termolecular reaction, say, the oxidation of nitric oxide, it is necessary to postulate a model for the activated complex. An example of such a model is given in Fig. 8.7. With such a structure, one must assume the possibility of internal rotation about the axis passing along the O—O bond. At a first approximation, the rotation may be considered to be free and the partition function can be evaluated from formula (5.107):

$$\frac{\left(8\pi^3 I_m kT\right)^{1/2}}{\sigma h}$$

where  $I_m$  is the reduced moment of inertia. It is understandable that in the presence of one degree of freedom of internal rotation

the number of vibrational degrees of freedom will diminish by unity and will be equal to 10. In accordance with this, the numerator of Eq. (8.43) for the rate constant will retain the product of ten terms expressing the vibrational partition functions of the activated complex, and there will appear a cofactor of the type (5.107) containing  $T^{\frac{1}{2}}$ . Therefore, now for the activation energy to be determined at absolute zero from experimental data as a function of 1/T, a somewhat modified expression of the type (8.47) must be employed to construct a graph. Namely,

$$\ln k_{\text{III}} + \ln \prod_{i=1}^{3} \left(1 - e^{-h\nu_i/kT}\right)^{-1} + 3 \ln T - \ln \prod_{i=1}^{10} \left(1 - e^{-h\nu^{\neq}/kT}\right)^{-1}$$
 (8.49)

A complete equation for the rate constant can be written down by calculating the constant coefficient, using the gram-molecular weights and expressing the moment of inertia in  $g \cdot \Lambda^2$  mole<sup>-1</sup> in the following form:

$$k_{111} = 5.12 \times 10^{16} \frac{T^{-3}g^{\neq}}{11g_{i}} \cdot \frac{(I_{A}I_{B}I_{C})^{1/2} I_{in}^{1/2}}{\sigma^{\neq} \prod_{i} (I_{i}/\sigma_{i})} \times \frac{\prod_{i=1}^{10} (1 - e^{-h\nu^{\neq}/kT})^{-1}}{\prod_{i=1}^{3} (1 - e^{-h\nu_{i}/kT})^{-1}} e^{-E_{0}^{\neq}/RT}$$

$$(8.50)$$

in which  $k_{\rm HI}$  is expressed in cm<sup>6</sup>·mole<sup>-2</sup>·sec<sup>-1</sup>.

The vibration frequencies in the activated complex are unknown. For a rough estimation at a first approximation they may be assumed to be equal to the experimentally observed frequencies of the stable molecule  $N_2O_4$ , all the frequency values exceeding 900 cm<sup>-1</sup> being omitted for calculations in a temperature range of 80-600 K. Taking into account the vibration, which is replaced by internal rotation, altogether seven frequencies of the molecule  $N_2O_4$  are left in the activated complex: 283, 380, 500, 600, 752, 813, and 831 cm<sup>-1</sup>. All the vibrational partition functions of the reactant molecules are practically equal to unity. Thus, in the grap'tical determination of the activation energy  $E_0^{\neq}$  as a function of the inverse temperature it will suffice to lay off the values of the following partition function:

$$\ln k_{III} + 3 \ln T - \ln \prod^{7} \left( 1 - e^{-hv^{\neq}/kT} \right)^{-1} = \ln k_{III} + f(T)$$
 (8.51)

The construction of the corresponding plot (Fig. 8.8) shows that the activation energy of the oxidation of nitric oxide is very close to zero since even a very small value of  $E_0^{\neq} = 200$  cal/mole gives a quite perceptible slope of the straight line. Thus, assuming

that  $E_0^{\neq} = 0$  and all the vibrational partition functions of the reactants are equal to unity and leaving only seven vibrational partition functions for the activated complex, we obtain a simplified expression for the rate constant:

$$k_{III} = \frac{5.12 \times 10^{16}}{T^3} \cdot \frac{g^{\neq}}{IIg_i} \cdot \frac{(l_A l_B l_C)^{1/2}}{\sigma^{\neq} \prod_i (l_i / \sigma_i)} \prod_i (1 - e^{-h\nu^{\neq}/kT})^{-1}$$
(8.52)

In this expression, the rate constant is explicitly inversely proportional to  $T^3$ , but this dependence must be eliminated by the

increase of the vibrational partition functions with temperature. As a result of this, the rate constant may pass through a minimum with rise of temperature. This is qualitatively confirmed by experiment: at 627 K the rate constant has a minimal value.

The moments of inertia of the activated complex are determined on the basis of the structure shown in Fig. 8.7 if the following internuclear distances are assumed: 1.22 for N=O, 1.32 for O-O, and 5 Å for

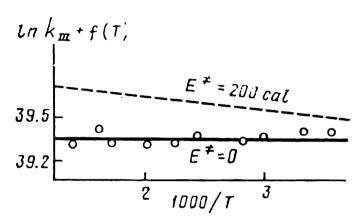


Fig. 8.8. Determination of the activation energy of the oxidation of nitric oxide according to the experimental rate constants and the assumed vibrational frequencies in the activated complex

N···O. In calculating the moments of inertia of total rotation, the complex was regarded as a rigid molecule, assuming that the internal rotation could not change the product  $I_{\Lambda}I_{\rm B}I_{\rm C}$  significantly. Substituting the numerical values into Eq. (8.52) yields:

$$k_{\text{III}} = \frac{3.2 \times 10^{17}}{T^3} \cdot \frac{g^{\neq}}{\Pi g_i} \prod_{i=1}^{7} \left(1 - e^{-iv\mathbf{v}^{\neq}/kT}\right)^{-1} \text{cm}^6 \cdot \text{mole}^{-1} \cdot \text{sec}^{-1}$$
 (8.53)

Here, obviously,  $g_i$  and  $g^{\neq}$  are the degeneracies of the electronic levels of the initial state (i.e., of two nitrogen molecules and an oxygen molecule) and the activated complex. Taking into account the ground state of the NO molecule ( ${}^2\Pi$ ) and the splitting of the levels  $g^{\neq}$  is evaluated to be 3.1 at ordinary temperature. The ground state of oxygen is a triplet state ( ${}^3\Sigma$ ). Therefore,  $\Pi g_i = 3 \times 3.1^2$ . The degeneracy of the electronic state of the activated complex is provisionally assumed to be equal to the degeneracy for the final system  $2NO_2$ , i.e., 4. Hence, with these assumptions,  $g^{\neq}/\Pi g_i = 4/28.8 = 1/7.2$ . The other assumptions, say,  $g^{\neq} = 1$ , as in the case of  $N_2O_4$ , do not alter  $k_{\Pi \Pi}$  by more than one

order of magnitude, and a higher accuracy cannot be claimed by the calculation.

The results of calculations for a number of temperatures are given in Table 8.3, where the observed rate constants are also presented. As seen, the calculated rate constants are in good agreement with the values found experimentally and this confirms the correctness of the basic propositions of the method and also the energy of activation close to zero. The decrease of the rate constant with rise of temperature is determined evidently by the presence of  $T^3$  in the denominator of the expression (8.53), but at high temperatures, as has already been said, the effect of the vibrational partition functions of the activated complex begins to predominate.

Analogous calculations for other reactions involving nitric oxide also lead to satisfactory results.

TABLE 8.3. The Rate Constants for the Oxidation of Nitric Oxide Calculated by Means of the Transition-State Theory and Obtained Experimentally,  $E_0^{\neq} = 0$ 

:111-10-9, cm <sup>6</sup> -11 ole-2-sec-1			111 <sup>-10</sup> -", em	6.mole - 2.sec -
nalculated fro.n (8.53)	obtained by experiment	Г. К	ealculated from (8,53)	obtained by experiment
86.0	41.8	413	2.2	4.0
16.2	20.2	564	2.0	2.8
5.3	10.1	613	2.1	2.8
3.3	7.1	662	2.0	2.9
	86.0 16.2 5.3	fro.n (8.53)         experiment           86.0         41.8           16.2         20.2           5.3         10.1	86.0 41.8 413 16.2 20.2 564 5.3 10.1 613	Second

4

It is necessary to note that the activated-complex theory (transition-state theory) is limited as regards the possibilities of calculation of the activation energy, though the potentialities of the theory in this respect are wide. This theory has made great advances, as compared with other theories, in the calculation of an important quantity contained in the rate constant—the pre-exponential factor of the Arrhenius equation. This refers to unimolecular and termolecular reactions and, especially, to bimolecular reactions.

The transition-state theory is beset by some serious difficulties which have not been discussed here.

## Kinetics of Chain Reactions

### 9.1. General Concepts

The two basic theories of chemical kinetics that have been so far considered, the theory of activated collisions and the transition-state theory, strive to solve the problem of the reaction rate on the basis of the concept of the elementary reaction act and to calculate, with the aid of statistical methods, the macroscopic velocity of a reaction consisting of numerous elementary acts.

In order to explain the kinetics of a rather large class of diverse reactions having numerous common features and extremely characteristic peculiarities, the concepts of the two theories are however insufficient. Here we mean reactions that proceed under the conditions of the interplay of elementary acts, as a result of which their observed velocity is not the outcome of simple summation. Among such reactions may be cited the so-called induced \* and, in the first place, chain reactions.

Chain reactions include the following classes of reactions:

I. The reactions of combustion and slow oxidation in the gas phase:

$$2H_2 + O_2 \longrightarrow 2H_2O$$

$$2CO + O_2 \longrightarrow 2CO_2$$

$$CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O. etc.$$

II. The various reactions involving hydrocarbons. For instance, decomposition reactions (the explosive decomposition of acetylene), numerous polymerization reactions, etc.

III. Many photochemical reactions, i.e., reactions effected by light absorption, such as the formation of IICl, HBr, COCl<sub>2</sub>,

etc.

IV. Finally, nuclear chain reactions, such as the decay of <sup>235</sup>U or plutonium in atomic piles or in atomic bombs.

<sup>\*</sup> For induced reactions, see the articles written by S. S. Vasiliev (see "Suggestions for Additional Reading" at the end of the book), where a different approach is proposed and the Semenov treatment adopted here is criticized.

Most of the reactions indicated above are characterized by certain common features which differentiate them from other reactions.

First, it should be noted here that the rate of these reactions is highly sensitive to the presence of certain impurities. For example, a mixture of hydrogen or carbon monoxide and oxygen reacts with difficulty if the gases to be mixed have been thoroughly dried. But the presence of water vapour in an amount corresponding to  $10^{-4}$  and  $10^{-5}$  mm Hg is sufficient for the reaction to pro-

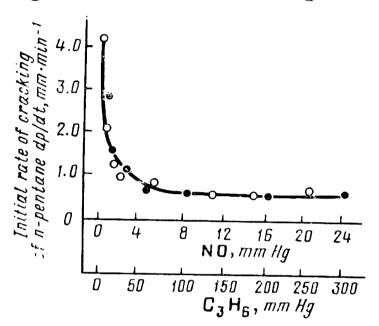


Fig. 9.1. The retarding effect of nitric oxide and propylene on the initial rate of the cracking of n-pentane (t = 530 °C, P = 100 mm Hg).

ceed with normal velocities. A mixture of hydrogen and chlorine does not react in the dark at room temperature, but it begins to react rapidly when small quantities of sodium vapour are introduced into the reaction mixture.

If the same reaction is initiated photochemically, the reaction is sharply slowed down by small amounts of oxygen: I per cent of O<sub>2</sub> lowers the rate of the formation of hydrogen chloride by about a thousand times. The thermal decomposition of many organic compounds,

say, ethers (dimethyl and diethyl ethers) and also of hydrocarbons (pentane) is retarded by addition of small amounts of nitric oxide. Frost and Dinzes have detected the retardation of the initial stage of the pyrolytic decomposition of hydrocarbons by addition of propylene. It is essential that in the cracking of a-pentane, the added amounts of nitric oxide and propylene slow down the reaction until the same limiting velocity is reached; this coincidence is shown in Fig. 9.1.

Since various impurities exert a quite characteristic retarding influence in the controlled chain decomposition of uranium, there arises the necessity of using high-purity materials, say, a neutron retarder, graphite. The action of rate-controlling cadmium rods (called moderators) introduced into the reactor may also be considered from the viewpoint of retardation by impurities.

So, the first specific feature is the high sensitivity of the rate of the class of reactions under consideration to the presence of impurities which can either initiate and accelerate or retard these reactions.

The rate of many gas reactions is affected by the presence of solid surfaces present. The reactions are most frequently slowed down by the walls of reaction vessels; reactions proceed more slowly in narrow than in wide vessels. In such cases, one speaks of the effect of the ratio of the surface area of the vessel, S, to its volume, V, on the rate of the reaction. In accordance with

what has been said above, ordinarily gaseous reactions of the type in question are retarded by increasing the ratio S/V. This ratio can be changed in practice by introducing, into the vessel, fragments of the vessel quartz, material—glass, celain. If the reaction in the vessel filled by such fragments (the ratio S/V is greater) proceeds more slowly, this is an indication, though not unambithat it belongs guous, chain reacthe category of tions.

In oxidation reactions in the gas phase, the fast reaction, the spontaneous combustion, is often accomplished only within definite limits of pressure and temperature. The graphical representation of the relations thus observed is called the **combustion peninsula** (or the ignition peninsula). Figure 9.2

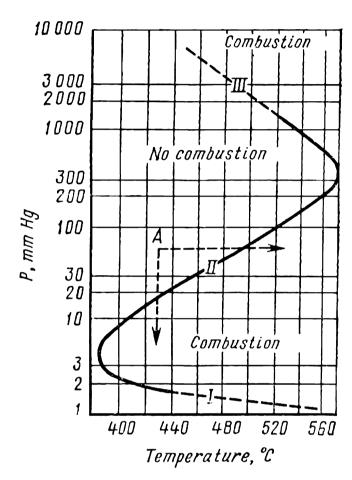


Fig. 9.2. The combustion peninsula for the oxidation of hydrogen

The three combustion limits: *I*—lower limit; *III*—the third or the mal limit.

gives data on the oxidation of hydrogen. By the way, a similar picture is observed in other cases too, say, in the oxidation of phosphorus, hydrogen sulphide, phosphine, silane and carbon monoxide vapours.

The ignition of oxyhydrogen gas occurs only under the conditions corresponding to the points within the boundaries of the combustion peninsula. Beyond the boundaries of the peninsula, no combustion takes place: the reaction proceeds slowly or does not occur at all. Starting from point A (Fig. 9.2), the combustion of the mixture can be induced by heating it (the arrow pointing to the right) until a state corresponding to points inside the peninsula is attained. More surprising and paradoxical at first sight was the fact that the combustion can be induced by lowering the pressure of the mixture (the arrow directed downward). True,

the subsequent decrease of the pressure will lead to the intersection of the representative point of the lower limit (*I* in Fig. 9.2) and to the emergence of the system from the combustion region.

Properly speaking, the existence of the lower combustion limit was first detected for another system—phosphorus vapour and oxygen. The very first observations were made by the French scientist Joubert in 1874, but they were forgotten. In the period 1926-1927 the Soviet scientists Semenov, Khariton, Val'ta, and Shal'nikov found that if the oxygen pressure is lower than a certain minimal value, the phosphorus vapour does not burn, and even the traces of the reaction cannot be detected. But as soon as the oxygen pressure limit is exceeded, combustion takes place. This phenomenon seemed so surprising that one of the most eminent specialists in the field of chemical kinetics, Bodenstein, suspected an experimental error and stated that the data obtained were in discord with the foundations of science. The data were, however, confirmed and, as was found later, they contradicted not the scientific foundations but the old conceptions. The other facts were also thought to be surprising. Thus, it turned out that the minimum oxygen pressure required for combustion was further decreased when an inert gas was added to the oxyhydrogen gas. Thus, the added amounts of argon increased, as it were, the reactivity of oxygen. The minimal oxygen pressure also decreased with increasing dimensions of the reaction vessel.

Later, when studying the hydrogen-oxygen system, Hinshel-wood discovered the existence of the upper combustion limit (11, Fig. 9.2). The contours of the peninsula were finally delineated and similar phenomena were established for a large number of other cases of oxidation reactions.

It is also characteristic that in the self-ignition region the fast reaction starts not instantly, as a rule, but upon the lapse of a certain time interval called the induction period \*, the length of which for the oxidation of hydrogen is tenths of a second.

All the specific features of the class of reactions in question are accounted for by the theory of chain reactions, an impetus to the development of which was given in 1913 when Bodenstein introduced the concept of the chain reaction.

A distinction is mainly made between two types of chain reaction: linear (non-branching) and branching chain reactions (or branched chain reactions). An example of a linear chain reaction is the formation of hydrogen chloride from hydrogen and chlorine:

$$H_2 + Cl_2 \longrightarrow 2HCl$$

The term induction period has already been encountered in the text in connection with consecutive reactions. It is also used in describing the autocatalysis phenomena.

It will be more graphic if we demonstrate the phenomena that arise here by reference to the photochemical method of initiating this process. As known, a mixture of hydrogen and chlorine does not practically react in the dark at room temperature and explodes upon illumination.

In photochemistry (for more detail, see Chapter 10) there is known the law of photochemical equivalence which states: When one quantum of light energy is absorbed by the reacting system,

one (and only one) molecule undergoes primary change.

Further, the main characteristic of a photochemical reaction is the total quantum yield  $\gamma$  given by the relation

$$\gamma = \frac{\text{number of molecules reacted}}{\text{number of quanta absorbed}}$$

If it is assumed that to the primary change of the molecule, which was meant in the Einstein law, there may correspond its chemical conversion, then the total quantum yield cannot be greater than unity. It has however been found in practice that the quantum yields of this reaction are very great; under favourable conditions they reach the value 10<sup>5</sup>. To reconcile this result with the undoubtedly correct Einstein law, Nernst suggested the following mechanism of the material \* chain:

$$Cl_2 \longrightarrow Cl + Cl$$

This reaction of dissociation of chlorine molecules into free atoms which are known to possess enhanced reactivity is the process of **chain initiation.** Generally speaking, it can be effected in various ways. For example, upon absorption of light:

$$Cl_2 + hv \longrightarrow Cl + Cl$$

It can also be accomplished thermally, upon collision, say, of two chlorine molecules:

$$Cl_2 + Cl_2 \longrightarrow Cl + Cl + Cl_2$$

Here the arrow above the chlorine molecule signifies an enhanced energy content consumed for dissociation.

The chain can also be initiated by chemical means, upon interaction, say, with a sodium atom, when its vapour is introduced:

$$Cl_2 + Na \longrightarrow NaCl + Cl$$

The process of chain initiation is followed by the chain itself:

$$CI + H_2 \longrightarrow HCI + H$$
  
 $H + CI_2 \longrightarrow HCI + CI$  chain steps I and II

<sup>\*</sup> The chain meant by Bodenstein is an energy chain.

The first of the elementary reactions written above gives rise to a free hydrogen atom which readily enters into reaction with a chlorine molecule. The second elementary reaction leads to the regeneration of the chlorine which starts off the next chain step (the chlorine and hydrogen atoms in all these reactions are chain centres):

and so on.

As a result, there is created a "chain" of reactions (propagation reactions), which under favourable conditions, for example, in the absence of oxygen, may involve many thousands of individual chain steps. Thus, per one primarily activated (say, under the action of light) molecule there are formed not two molecules of HCl, as was the case with an ordinary bimolecular mechanism, but hundreds of thousands. The following is characteristic of the reaction chain indicated: in a chain step, per one active particle, H or Cl, that enters into reaction there appears another reactive particle. It is such reaction chains that are called linear or non-branching.

Apart from the chain initiation and propagation reactions given above, the following processes may also occur in the reacting system:

$$H + H + M \longrightarrow H_2 + M$$
  
 $H + H + S \longrightarrow H_2 + S$   
 $Cl + Cl + M(S) \longrightarrow Cl_2 + M(S)$   
 $H + Cl + M(S) \longrightarrow HCl + M(S)$ 

where M and S denote a third particle or the wall of the reaction vessel (these are collectively termed a third body). These reactions remove the activated particles from the system, as a result of which the chain ceases to grow and is "broken" or, as is usually said, the chain is terminated; such reactions are known as **chain termination reactions**.

The number of steps in a reaction chain is called its length. Generally speaking, when the reaction proceeds, say, the formation of hydrogen chloride, in the system there are developed chains of the various lengths, from very short to very long. Nonetheless, under given conditions, the reaction may be characterized by the average chain length v which depends on a very large number of factors: temperature, pressure, impurities, the shape of the reaction vessel and the condition of its walls, etc. It is the average chain length which is evidently determined by experiment. The most straightforward method of measuring the chain length of a photochemical reaction is the determination of the

quantum yield  $\gamma$ , which at a first approximation is equal to  $\nu$ . In thermal reactions, say, in the decomposition of organic compounds, the chain length can be evaluated by the method of reaction inhibition by traces of other substances which are usually referred to as **inhibitors** or **retarders** (NO).

We shall present here, as an example, the data obtained by Gibbs on the inhibition of the thermal decomposition of the die-

thyl ether vapour by nitric oxide at 504 °C. Table 9.1 lists data referring to the initial pressure of the ether, 200 mm Hg.

As seen from Table 9.1, the rate of the reaction is rather sharpdiminished with increasing amount of nitric oxide added and at  $p_{NO} = 1.12$  mm Hg the ratio \*  $w_0/w = 3.5$ . As the concentration of nitric oxide increases further the rate tends to a constant value  $(w_{\infty})$ . Since, according to the Hinshelwood interpretation, the retardation is associated with the suppression of the chain reaction, and the limiting velocity  $w_{\infty}$  corresponds to the development of the reaction in the absence of chains, the ratio  $w_0/w_\infty$  may equated to the chain length of the uninhibited reaction. In this particular case, the chains rather short,  $v \approx 4.5$ . It is essential that in the decomposition of ethers (diethyl ether and others)

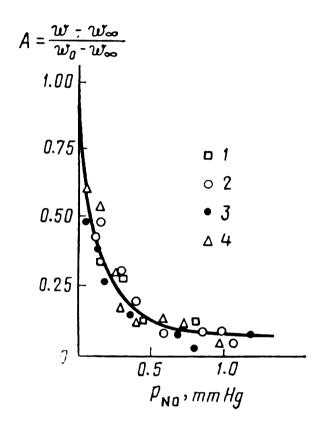


Fig. 9.3. The degree of inhibition (A) of the thermal decomposition of diethyl ether against the pressure of nitric oxide, t = 504 °C. The initial pressure of ether: t = 51; t = 2-103; t = 3-200; t = 4-400 mm Hg safter J. E. Hobbs).

the average chain length is independent of the ether pressure. This is evidenced by the plot in Fig. 9.3 which shows that the degree of inhibition

$$A = \frac{w - w_{\infty}}{w_0 - w_{\infty}}$$

is independent of the ether pressure.

In the interpretation of the results it is assumed that the process of removal of the chain-propagating radical by nitric oxide competes with another, chain-terminating reaction which is prac-

<sup>\*</sup> Here the following notation is adopted:  $w_0$  is the rate in absence of nitric oxide; w is the rate in the presence of a given amount of nitric oxide; and  $w_\infty$  is the rate of the completely inhibited reaction.

Reaction rate w, mm·sec — 1·10 <sup>3</sup>	Degree of inhibition A *	Amount of NO, mm Hg	Reaction rate w, num·sec - 1·10 <sup>3</sup>	Degree of inhibition A*
68.8	1.000	0.409	23.6	0.146 0.088
37.6	0.415	0.765	17.4	0.027
29.8	0.215	1.120 ∞	19.6 16	0.061 0.000
_	rate w. mm·sec <sup>-1</sup> ·10 <sup>3</sup> 68.8 41.4	rate w, min·sec - 1.103 Degree of inhibition A *  68.8 1.000 41.4 0.488 37.6 0.415	Tate w, mm·sec - 1.103     Degree of inhibition A * NO, mm Hg       68.8     1.000     0.409       41.4     0.488     0.582       37.6     0.415     0.765       29.8     0.215     1.120	rate $w$ , mm·sec $^{-1} \cdot 10^3$ Amount of NO, mm Hg       rate $w$ , mm·sec $^{-1} \cdot 10^3$ 68.8       1.000       0.409       23.6         41.4       0.488       0.582       20.6         37.6       0.415       0.765       17.4         29.8       0.215       1.120       19.6

TABLE 9.1. Inhibition of the Thermal Decomposition of Dietnyi Lt., by Nitric Oxide. The Ether Pressure is 200 mm Hg, t = 504 °C

tically independent of the ether concentration. No chain termination occurs at the walls since the increase of the ratio S/V (the experiment with the "filled" vessel) has no substantial influence on the reaction velocity. Therefore, the reaction leading to the termination of the chain is a unimolecular dissociation of the active radical. The supposed mechanism of the chain reaction consists of the following steps:

(1) 
$$C_2H_5OC_2H_5 = CH_3 + CH_2OC_2H_5$$
  
A R S

(2) 
$$CH_3 + C_2H_5OC_2H_5 = C_2H_6 + CH_2OC_2H_5$$

$$(3) \quad CH_2OC_2H_5 = CH_3 + CH_3CHO$$

(4) 
$$CH_3 + CH_2OC_2H_5 = product$$

(5) NO + 
$$CH_2OC_2H_5 = product$$

Using the steady-state method (see Sec. 3.6), we can write

$$\frac{d[R]}{dt} = k_1[A] + k_3[S] - k_2[R][A] - k_4[S][R] = 0$$
 (9.1)

and

$$\frac{d[S]}{dt} = k_1[A] + k_2[R][A] - k_3[S] - k_4[R][S] - k_5[S][NO] = 0$$

From these steady-state conditions we have

$$[R] = \frac{-k_2 k_5 [NO] + \{(k_2 k_5 [NO])^2 + 8k_2 k_1 (k_1 k_5 [NO] + 2k_1 k_3)\}^{\frac{1}{2}}}{4k_2 k_4}$$
(9.2)

As has already been noted, apart from a chain reaction, there also takes place the unpoisoned process of decomposition, perhaps also at the wall of the reaction vessel. We shall denote the

<sup>\*</sup>  $A = (w - w_{\infty})/(w_0 - w_{\infty}).$ 

rate of this reaction by k'f(A). The overall rate of the reaction  $w = k'f(A) + k_2[R][A]$ 

where the second term on the right-hand side is the rate of the poisoned chain reaction. Or, substituting [R] from Eq. (9.2),

$$w = k' \int (A) + \frac{k_2 [A]}{4k_2 k_4} \left[ \left\{ (k_4 k_5 [NO])^2 + 8k_2 k_4 (k_1 k_5 [NO] + 2k_1 k_3) \right\}^{1/2} - k_1 k_5 [NO] \right]$$
(9.3)

If no nitric oxide is present and [NO] = 0, then

$$w_0 = k' f(A) + \frac{k_2 [A]}{4k_2 k_4} (16k_1 k_2 k_3 k_4)^{1/2}$$
 (9.4)

Thus, the rate of the uninhibited chain reaction is first order with respect to the concentration (pressure) of the ether according to experiment. If the pressure of nitric oxide is high, the reaction rate is equal to the limiting value corresponding completely to the inhibited process:

$$w_{\infty} = k' \int (A)$$

From relations (9.3), (9.4), and (9.5) it is easy to find the so-called degree of inhibition:

$$A = \frac{w - w_{\infty}}{w_{0} - w_{\infty}} = \frac{\{(k_{2}k_{5} [NO])^{2} + 8k_{2}k_{4} (k_{1}k_{5} [NO] + 2k_{1}k_{3})\}^{1/2} - k_{1}k_{5} [NO]}{4 (k_{1}k_{2}k_{3}k_{4})^{1/2}} = \{(\alpha [NO])^{2} + \beta [NO] + 1\}^{1/2} - \alpha [NO]$$
(9.6)

where  $\alpha = k_2 k_5 / 4(k_1 k_2 k_3 k_4)^{1/2}$  and  $\beta = k_5 / 2k_3$ .

Hence, according to experiment, the degree or amount of inhibition A does not depend on the ether concentration (Fig. 9.3). The experimental data are well described by a theoretical curve calculated from the simplified formula:

$$A = \{ (\alpha [NO])^{1/2} + 1 \}^{1/2} - \alpha [NO]$$
 (9.7)

since the term  $\beta$  [NO] is small.

From Eqs. (9.4) and (9.5) we can also calculate the average chain length:

$$v = \frac{w_0}{w_\infty} = \frac{k'f(A) + [A](k_1k_2k_3k_4)^{1/2}}{k'f(A)}$$
(9.8)

Since, according to experiment, k'f(A) is proportional to [A], it turns out that v is independent of the ether concentration.

Analogous investigations have been carried out also on the inhibition of the thermal decomposition of hydrocarbons by nitric oxide, in particular, of ethane. Essentially different results have been obtained: the most important difference is due to the fact

that for hydrocarbons the chain length depends on the concentration (pressure) of decomposed hydrocarbons. Below are given some data for ethane, which have been obtained at 600 °C:

Pressure of ethane, mm	Average chain length
57	9.8
100	6.9
300	5.9
454	4.1

As seen, in this case the chain length decreases with increasing concentration (pressure) of the reagent and it does so approximately in proportion to  $[C_2H_6]^{1/2}$ . The difference in behaviour between hydrocarbons and ethers is accounted for by the different functions of nitric oxide in the chain termination processes. In the first case, NO removes a radical of type R, which propagates the chain, whereas in the second case a radical of type S is removed, which itself does not propagate the chain but gives rise to a **chain carrier** (also called a *chain propagator*) when it is decomposed. On the basis of the chain mechanism described here we can

On the basis of the chain mechanism described here we can ascertain many of the specific features of the class of reactions under discussion, for example, the influence of the substances added. It is clear that a small amount of added substances contributing to the initiation of a chain, say, sodium vapour in a mixture of hydrogen and chlorine, can produce a very great effect since per each atom of the added substance after the step

$$Cl_2 + Na \longrightarrow NaCl + Cl$$

there can react, on an average, up to hundreds of thousands of hydrogen and chlorine molecules.

The action of inhibitors may be as strong. The molecule of an inhibitor, say, of oxygen, in the reaction between hydrogen and chlorine, captures the hydrogen atom

$$H + O_2 + M \longrightarrow HO_2 + M$$

and, having formed the slightly active radical  $HO_2$ , can terminate the chain at the very beginning and thus reduce the amount of reaction products also by a hundred thousand times.

Owing to this mechanism, we can also explain the retardation of the reaction when the ratio of the surface to the volume of the vessel increases. It is known that reactions of the type of the recombination of hydrogen atoms do not practically proceed by the bimolecular mechanism but are accomplished by a triple collision or at the wall of the vessel. The activated particles, diffusing to the wall, are destroyed on it and the chains are terminated:

$$H + H + S \longrightarrow H_2 + S$$

The role of the walls of the reaction vessel must especially increase at low pressures of the reacting gases when the diffusion of the activated particles to the walls is facilitated due to the decrease of the number of collisions. This is supported by experiment. That the effect of the walls is reduced with increasing size of the vessel (the decrease of the ratio S/V) is thought to be natural—it is precisely this factor that is responsible for the decrease of the minimum required oxygen pressure in the combustion of phosphorus vapour mentioned above. Addition of an inert gas which does not directly participate in the reaction (He, Ar, Ne) but which prevents the diffusion of the activated particles to the walls must also impede the chain termination on the walls. We have earlier mentioned the decrease of the minimum oxygen pressure on addition of argon to a mixture of phosphorus vapour and oxygen.

At high pressures of the gas in the reacting system the diffusion to the walls is hindered and the chain termination on the walls does not play a significant part. But the increase of the pressure enhances the role of triple (three-body) collisions in the bulk, which also lead to the destruction of the activated particles and to a chain termination. To this category belong processes of the type

$$H + H + M \longrightarrow H_2 + M$$

that is, the recombination of atoms and simple radicals and also the above-mentioned formation of the radical  $HO_2$ . In fact, with the aid of formulas (6.27) and (6.48), it can be shown how the ratio of ternary to binary collisions increases with increasing pressure:

ø, mm Hg	$Z_8/Z_2$
0.2	$10^{-6}$
2	$10^{-5}$
20	10-4
200	$10^{-3}$
2000	$10^{-2}$

If at a pressure of 0.2 mm Hg there is one three-body collision per one million two-body collisions, then at 2000 mm Hg there will be one three-body collision per only 100 two-body collisions. The ratio  $Z_3/Z_2$ , as can easily be seen, increases in proportion to the gas pressure. Therefore, as the pressure increases the role of three-body collisions in chain termination is enhanced.

It is precisely the chain termination on the walls and in the bulk that accounts for the existence of the combustion limits (I and II) and of the entire ignition peninsula similar to that shown in Fig. 9.2. In this case, however, both the limits and the penin-

sula refer to chain reactions of a different type, namely, to branching chains characteristic of self-accelerating oxidation reactions. In the case of the formation of HCl, as has already been mentioned, during the chain propagation processes, for one particle entering into reaction there is formed also one particle of a different species:

$$|C| + H_2 \longrightarrow HCl + |H|$$

A different situation arises during the chain propagation in explosive reactions. For instance, in the oxidation of hydrogen—the reaction of oxyhydrogen gas—the following sequence of elementary processes is thought to be quite substantiated \*:

(0') 
$$H_2 + O_2 \longrightarrow 2OH$$
  
 $H + HO_2$   
(0")  $H_2 + M \longrightarrow H + H + M$   
(0"'')  $O_2 + O_2 \longrightarrow O_3 + O$   
(1)  $OH + H_2 \longrightarrow H_2O + H$   
(2)  $H + O_2 \longrightarrow OH + O$   
(3)  $O + H_2 \longrightarrow OH + H$   
(4)  $2H + wall \longrightarrow H_2 + wall$   
(5)  $OH + H + wall \longrightarrow H_2O + wall$   
(6)  $H + O_2 + M \longrightarrow HO_2 + M$ 

The first group of elementary reactions are rare processes of chain initiation, the formation of activated particles—free atoms II and O or the radical OH. The second group includes chain propagation and branching processes. In reactions 2 and 3, instead of one atom entering into reaction, there appear two activated particles, one of which can continue the chain and the other can start off a new chain. This is what we call chain branching. If it takes place frequently, then even one initially created chain can bring about the development of many chains. In the limiting case, it may be thought that branching occurs in each step and then one speaks of an entirely branching-chain reaction. In other cases, branching can occur less frequently. When branching takes place frequently, the development of a chemical reaction may become avalanche-like; such a process is depicted schematically in Fig. 9.4. In this case, the rate of the reaction, even with an originally small number of activated particles or of primary chains, may rapidly increase and the process will end with ignition or explosion. This is what exactly happens inside the combustion

<sup>\*</sup> Though this mechanism was given at the beginning of the book, the author thinks it expedient to cite it here again.

region (see Fig. 9.2). The lower and upper combustion limits can be qualitatively explained as follows. At pressures lower than those corresponding to the lower limit, activated particles readily diffuse to the walls of the vessel, where they are destroyed. The chain termination on the walls predominates over the branching and no fast reaction is developed. As the pressure increases the diffusion to the walls becomes more and more strongly hindered, and the number of two-body collisions of types 2 and 3 (page 254), which lead to chain branching, increases. At pressures exceeding a certain critical value (the lower limit I) the chain initiation and branching begin to predominate over the termination. As a result, the reaction self-accelerates and may end up with combustion

or explosion. It is believed that exactly this phenomenon occurs inside the combustion peninsula.

As the pressure increases further due to the increasing role of three-body collisions, chain termination processes in the bulk become more and more significant. In the oxidation of hydrogen, an important part is played by reaction 6 leading to the formation of the slightly activated radical HO<sub>2</sub>.

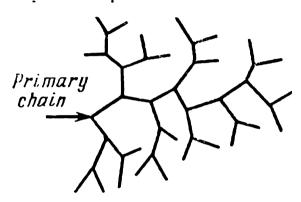


Fig. 2.4. The avalanche-like development of a chain reaction.

If the pressure exceeds the value corresponding to the upper limit (II in Fig. 9.2), chain termination predominates over chain propagation and the possibility of a fast reaction being developed disappears.

The induction period that precedes the ignition of the combustible mixture inside the peninsula is accounted for by the theory of branching-chain reactions as follows. First, the number of chains may be very small and the reaction proceeds slowly because of the insufficient sensitivity of the analytical methods. But, upon the lapse of a certain period of time,  $t_{\rm ind}$ , the number of chains increases enormously because of the avalanche-like propagation mentioned above, which is followed by combustion or explosion. Theory gives the following relationship between reaction velocity and time for this case:

$$w = A\left(e^{q \cdot t} - 1\right) \tag{9.9}$$

in which A and  $\varphi$  are constants characterizing the reaction and dependent on a number of conditions, and t is the time. Graphically, the function (9.9) is presented in Fig. 9.5. When analysing this figure it should be kept in mind that in the derivation of w = f(t) the decrease of the concentration of starting substances due to combustion has not been taken into account, and therefore

no physical significance should be ascribed to the tendency of the reaction rate to increase to infinity with time. The reaction velocity becomes very great but not infinite. We may also note some uncertainty of the concept of the induction period which may formally be defined as the time during which the rate of the reaction increases by a factor of e times; the experimental determination of the duration of the induction period,  $t_{\rm ind}$ , actually depends

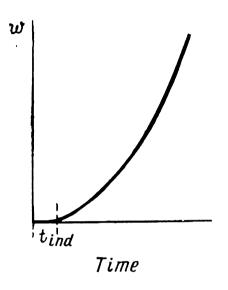


Fig. 9.5 The time dependence of the rate of a branching-chain reaction inside the combustion peninsula.

on the sensitivity of the instrument, say, of the membrane manometer and the recorder connected to it.

Thus, the chain mechanism can account for many specific features of the class of reactions under discussion. The development of the theory of branching-chain reactions has been largely due to the Semenov school and the English school of Hinshelwood. This theory played a very important part at a later time in the accomplishment of the chain decomposition of uranium and other radioactive elements.

Figure 9.2 also gives the third combustion limit which lies in the region of higher pressures. In most cases, the existence of this third limit is evidently associated with the occurrence of a thermal ex-

plosion, though the possibility of a chain combustion is not excluded under certain conditions at high pressures.

### 9.2. Elementary Probability Theory of Chain Reactions

In general, two variants of the theory of chain reactions are meant here: a rigorous theory based on the solution of simultaneous differential equations, and the other, less rigorous, though incomparably more spectacular, probability theory. In this section we shall be concerned with the discussion of the second variant.

We have already introduced the concept of the average chain length v. It will be recalled that v is the average number of elementary reactions induced by one active particle (an atom or radical) generated originally by some independent means, say, photochemically. Let the number of such particles generated independently per unit time in unit volume be  $n_0$ . Obviously,  $n_0$  may be called the **rate of chain initiation**.

The inverse quantity will be called the **probability of chain termination**  $\beta$ . This interrelation can be explained with the aid of a schematic representation of the development of a chain reaction

in time, such as that shown in Fig. 9.6. The dots signify the appearance and regeneration of an active particle, and the cross denotes the destruction of a particle in any chain step, i.e., its termination. The probability of chain termination is defined as the ratio of the number of favourable events to their total number. In the case under consideration, for one favourable contributing event, the termination, there are altogether  $\nu$  events. Hence, the

probability of termination \*

$$\beta = \frac{1}{2} \tag{9.10}$$

We shall further assume the possibility of a chain propagation step—the appearance in any chain step of two or more particles instead of one active particle propagating the chain. In an analogous manner, we shall define the probability of chain propa-

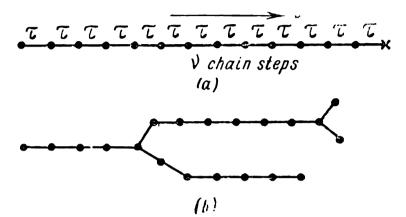


Fig. 9.6. Schematic representation of the reaction chain:

(a) - non-branched chain; (b) - branched chain.

gation  $\delta$ . We introduce some other definitions and designations. Let  $\tau$  denote the time during which there occurs, on an average, one chain step. Thus, the product  $v\tau$  will define the average time of chain development from the moment of initiation to chain termination. The concentration of active particles, i.e., the number of activated particles contained in unit volume will be n. The rate of change of the concentration of particles will evidently be expressed by the difference in the rate of their formation and disappearance. Let us dwell in some detail on the rate of disappearance. If the chain length is v=1, i.e., there are, properly speaking, no chains, the particle is destroyed in each chain step. Then, during the time  $\tau$ , which has been defined as the time of development of one chain step, there will react all n particles present, and the rate of disappearance will be equal to

$$\frac{n}{\tau}$$
 particles/cm<sup>3</sup> · sec

But if the chains are developing and their average length is equal to  $\nu$ , the particle will be regenerated, on an average,  $\nu$  times and will be destroyed only after the time  $\nu\tau$  is elapsed. Hence, the rate of decrease of the concentration of particles will now be expressed by the relation

$$\frac{n}{v\tau} = \beta \frac{n}{\tau}$$

<sup>\*</sup> Strictly speaking, 1/(v-1) but it must be assumed that  $v \gg 1$ .

Further we shall take into account the possibility of a branching process, i.e., let  $\delta$  be greater than zero. The effect of branching may be approximately taken into consideration by assuming that it operates as if in the direction opposite to the termination or, in other words, it lengthens the chains and reduces the probability of termination to  $\beta - \delta$ . Thus, the rate of change of the concentration of activated particles, w, may be finally written as follows:

$$\frac{dn}{dt} = n_0 - (\beta - \delta) \frac{n}{\tau} \tag{9.11}$$

Separating the variables and integrating by parts on condition that at the start of the reaction t = 0 and n = 0, we obtain the time dependence of n:

$$n = \frac{\tau n_0}{\beta - \delta} \left( 1 - e^{-\frac{\beta - \delta}{\tau} t} \right) \tag{9.12}$$

Now we can determine the reaction velocity, i.e., let us say, the rate of increase of the concentration of product molecules. Since in one chain step, i.e., during time  $\tau$ , there will appear one molecule, the total number of molecules formed in unit volume per unit time will be  $n/\tau$ . Thus, the rate of reaction will be expressed by the relation

$$w = \frac{n}{\tau} = \frac{n_0}{\beta - \delta} \left( 1 - e^{-\frac{\beta - \delta}{\tau t}} \right) \tag{9.13}$$

This is exactly the basic equation of the variant of chain theory under discussion; several cases should be considered in the analysis of this variant. In the simplest case, it may be assumed that no branching is involved, i.e.,  $\delta = 0$ . Then, evidently, relation (9.13) will become:

$$w = v n_0 \left( 1 - e^{-\frac{\beta}{\tau} t} \right) \tag{9.14}$$

As shown in Fig. 9.7, the reaction rate must increase from the start of the reaction and reach a limiting value equal to  $vn_0 = n_0/\beta$ . In other words, in this case the system must attain a steady state in which the rate is constant. This steady-state rate, due to the presence of chains, is v times greater than the rate of initiation of reaction acts,  $n_0$ , i.e., the reaction rate in the absence of chains (v = 1).

In another, intermediate case, suppose we have the finite probability of branching but its numerical value is lower than the probability of termination, i.e.,  $0 < \delta < \beta$ . This ratio of probabilities also leads to the attainment of a steady-state rate, which will be greater than in the first case, namely,  $n_0/(\beta - \delta)$ . In all this reasoning, it should be remembered that here we are concerned

with the idealized conditions of the development of the reaction—the concentrations of reactants are kept constant and the reaction products are removed from the reaction zone. As a matter of fact, when the reaction is conducted, for example, in a closed vessel, the rate will pass through a maximum due to the "burning-off" of the reactants; this is shown in Fig. 9.7 by dotted lines. Here, it may even happen so that the stationary-state value will

not be reached at all: the maximum rate will be lower than the steady state rate

the steady-state rate.

An entirely different picture will obtain if the probability of a branching process is found to be greater than the probability of termination, i.e.,  $\delta > \beta$ . Then, formula (9.13) may be rewritten thus:

$$w = \frac{n_0}{\delta - \beta} \left( e^{+\frac{\delta - \beta}{\tau} t} - 1 \right) =$$

$$= A \left( e^{\varphi t} - 1 \right) \approx A e^{\varphi t} \quad (9.15)$$

where A and  $\phi$  are positive constants. Formula (9.15) coincides with formula (9.9). The

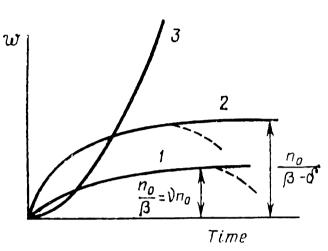


Fig. 9.7. The time dependence of the rate of a chain reaction:

1-no chain branching; 2-probability of branching is lower than the probability of termination  $(0 < \delta < \beta)$ ; 3-probability of branching is greater than the probability of termination  $(\delta > \beta)$ .

positive power function of in it of a indicates the possibility of infinite acceleration of the reaction, i.e., the development of chain combustion or explosion. As has already been said, one should not look for a disagreement between the real process and the formal tendency of the reaction velocity toward infinity in relations (9.9) and (9.15). Taking account of the changing conditions and, in the first place, of the combustion of the reactants would have shown a very great but not infinite velocity. Perhaps, it would be superfluous to remind that within the boundaries of the combustion peninsula there are just realized conditions when  $\delta > \beta$ , and outside the peninsula the conditions correspond to the inequality  $\beta > \delta$ . Thus, the theory of branching-chain reactions accounts quantitatively for the existence of the lower and upper combustion limits.

Equation (9.13) is sometimes \* written in a somewhat different form, introducing the notations  $(\beta - \delta)/\tau = g - f$  and  $1/\tau = a$ :

$$w = \frac{an_0}{g - f} \left( 1 - e^{-(g - f) t} \right) \tag{9.16}$$

<sup>\*</sup> Semenov, N. N., Some Problems in Chemical Kinetics and Reactivity, Princeton University Press, Princeton, N. J., 1958.

Here the factor a, equal to the reciprocal value of the average time of occurrence of one chain step, characterizes probably the rate of chain propagation. The quantities g and f, which have the dimensions inverse to time, remain, under given conditions, to be proportional to the probabilities of the termination proper and branching of the chain, respectively. If f = g, then, as can easily be seen, the rate of the reaction will be proportional to time

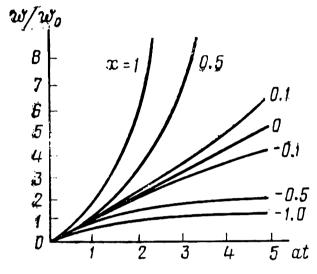


Fig. 9.8. The dependence of the apparent chain length  $v = w/w_0$  on the dimensionless coordinate  $at = t/\tau$  at various ratios of (f-g)/a = x (after Nalbandyan and Voevodsky).

after the indeterminate form is evaluated,

$$w = an_0 t \tag{9.17}$$

and the process ceases to be steady-state, though at small  $n_0$  the increase may be slow and will not lead to combustion. At f > g Eq. (9.16) turns into an analog of relation (9.15). Namely,

$$w = \frac{an_0}{\int -g} \left( e^{(f-g)t} - 1 \right)$$
 (9.18)

For the purpose of graphical illustration of the effect of the difference f - g, we take into account that in the absence of chains the reaction velocity is equal to  $n_0 = w_0$ , i.e., to the rate of generation

of active particles, therefore the ratio  $w/w_0 = w/n_0$  may be regarded as the average chain length, or better, the apparent chain length with all chain branchings being taken into consideration. If we introduce the notation (f-g)/a = x, then expression (9.18) will be represented in the form

$$v = \frac{w}{w_0} = \frac{1}{x} \left( e^{xat} - 1 \right) \tag{9.19}$$

In Fig. 9.8 the dependence of the ratio  $w/w_0$  is represented in the form of a function of a dimensionless coordinate at (with respect to time) at different values of x, which is proportional to the difference between the probabilities of chain branching and termination. At x=0 the ratio  $w/w_0$  increases in accordance with Eq. (9.17) in proportion to time. With negative values of x the apparent chain length reaches a limit which is the lower the more negative the value of x. Finally, at x>0 the apparent chain length in the absence of burning-off would increase without limit, and if x is sufficiently large, the acceleration of the reaction caused by it will end up with combustion or explosion. Figure 9.8, in fact, repeats Fig. 9.7, but it provides a clearer picture of the

increase of the apparent chain length with time as the cause of combustion. This is exactly the chain combustion or explosion.

It is interesting, using numerical examples, to trace out the effect of various factors on reaction velocity or, more exactly, on the amount of substance reacted. If we compute the latter from the formula

$$y = \int_{0}^{t} wt \tag{9.20}$$

the result will be

at 
$$j - g < 0$$
  $y = \frac{an_0}{j - g}t$  (9.21)

at 
$$f - g = 0$$
  $y = \frac{an_0}{2}t^2$  (9.22)

at 
$$f - g > 0$$
  $y = \frac{an_0}{(f - g)^2} [e^{(f - g)t} - 1] - \frac{an_0}{2} t$  (9.23)

If the amount  $n_0$  of active particles generated independently per 1 sec in 1 cm³ is very small, then at f-g<0 the rate of the steady-state reaction will also be very slow. But if f-g>0 and  $a=1/\tau$  is very large, then even if  $n_0=1$  (only one active particle is formed per second in 1 cm³), then the rate may increase up to very large values. Suppose that f is large and is equal, for example, to 500, and at the same time let  $n_0$  be equal to 10. As regards f-g, let it vary from -5 to +5, which makes up  $\pm 1$  per cent (with respect to 500) of the variation in both directions from the condition f-g=0. To simplify the calculations, we also put f=a, i.e., we assume that branching occurs in each chain step (a completely branched chain;  $\delta=1$ ). Then, at f-g=-5 the steady-state rate will be equal to a negligible value:

$$w = \frac{an_0}{1 - g} = \frac{5 \times 10^2 \times 10}{5} = 10^3 \text{ molecules} \cdot \text{cm}^{-3} \cdot \text{sec}^{-1}$$

Since even at a pressure of  $0.01 \text{ mm Hg in 1 cm}^3$  there are contained more than  $10^{14}$  molecules, the rate will be found to be practically non-observable.

A slight change in the conditions, say, an increase in the pressure, when f-g=+5, leads to an entirely different situation. Thus, according to formula (9.16) the rate is equal to

$$w \approx \frac{an_0}{f - g} e^{(f - g) t} = 10^3 e^{5t}$$

and by time t = 5 sec it reaches a very large value of about  $10^{14}$  molecules  $\cdot$  sec<sup>-1</sup>. It is interesting that by the fourth second the amount of substance reacted will be still small. Indeed, by for-

mula (9.23) (the second term being omitted)

$$y = \frac{\int n_0}{(g - f)^2} e^{(f - g)t} = \frac{5 \times 10^2 \times 10}{25} e^{5t} = 9.7 \times 10^{10} \approx 10^{11}$$
 molecules

In other words, by the fourth second there will have reacted altogether only 0.1 per cent of the substance (p = 0.01 mm). By the fifth second there will have reacted

$$y = 2 \times 10^2 \times e^{25} = 2 \times 10^2 \times 10^{10.83} = 1.35 \times 10^{13}$$
 molecules

which makes about 14 per cent of the original amount of reactant. Then, the exponential function increases so rapidly that by time t=5.35 sec there will have reacted 80 per cent. Thus, in fact, the reaction starts and is complete in less than one second and will look like combustion.

Thus, the existence of the two combustion limits, the lower and the upper limit, is ascribed by the chain theory to the competition between termination and branching, the probabilities of which are differently dependent on the conditions. More detailed theories of these limits have also been developed, which permit quantitative calculations.

We have repeatedly mentioned above the third combustion limit sometimes referred to as the thermal limit (Fig. 9.2). It is believed that this limit is largely of thermal nature.

#### 9.3. Thermal Combustion (or Explosion)

The processes of self-ignition of combustible mixtures, which have been considered above and which are caused by the rapid development of branching chains, may be called isothermal since they can develop at constant temperature.

Combustion or explosion may however be caused by the self-heating of the reacting mixture, independently of the reaction mechanism. The reaction rate increases with rise of temperature by an exponential law and the rate of heat removal is slower. And if in an exothermic reaction the heat is not removed from the reaction zone at a sufficient velocity, the reaction mixture will begin to self-heat and the reaction will be accelerated faster and faster. As a result, combustion or explosion can occur. In such cases one speaks of thermal combustion.

To establish the conditions of thermal combustion it is evidently necessary to consider the thermal balance of the unit volume of the reacting system. Following Semenov's treatment, we shall do this, using, as an example, the general bimolecular reaction

$$A + B \longrightarrow C + D + Q$$
 cal/mole

Here, the heat evolved is considered to be positive in accordance with the thermochemical notations. We shall write the reaction

rate according to the elementary collision theory:

$$w = Z_0[A][B] e^{-E/RT} \text{ (mole} \cdot \text{cm}^{-3} \cdot \text{sec}^{-1}\text{)}$$
 (9.24)

Taking into account the reaction equation, we may represent the rate of heat evolution,  $q_1$ , in the following form:

$$q_1 = Qw = QZ_0 [A] [B] e^{-E/RT} (cal \cdot cm^{-3} \cdot sec^{-1})$$

Introducing for the binary mixture the mole fractions  $N_A$  and  $N_B = 1 - N_A$ , we express the concentrations of the reacting substances in terms of the total pressure P:

$$q_1 = \frac{QZ_0}{(RT)^2} N_A (1 - N_A) P^2 e^{-E/RT} = DN_A (1 - N_A) P^2 e^{-E/RT}$$
(9.25)

Though the coefficient D contains  $T^{-2}$ , it may be considered constant at a first approximation as compared with the power function. According to Eq. (9.25), the amount of heat evolved in unit

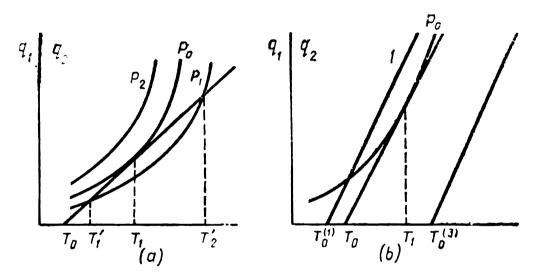


Fig. 9.9. The thermal balance of combustion:

(a)—the rate of heat evolution at pressures  $P_2 > P_0 > P_1$ ; the straight line is the rate of heat emission at the wall temperature  $T_0$ ; (b)—rate of heat evolution at the pressure  $P_0$ ; 1. 2, 3—rates of heat emission at various temperatures of the wall.

volume per unit time increases sharply with rise of temperature. The quantity  $q_1$  increases also with increasing total pressure. Figure 9.9 represents the curves of the rate of heat evolution versus temperature for three pressures:  $P_1 < P_0 < P_2$ . On the other hand, the amount of heat given off by the gas is proportional to the difference between the temperature of the gas, T, and that of the vessel wall,  $T_0$ :

$$q_2 = \varkappa \left( T - T_0 \right) \tag{9.26}$$

Here  $\varkappa$ , the total heat-transfer coefficient, depends on the shape of the vessel, the surface area of its walls, but it is independent of pressure. Therefore, at a given temperature of the wall the dependence of  $q_2$  on temperature is expressed by a straight line. If this

straight line is compared with the  $P_2$  curve, then it will become evident that the process cannot be steady-state: the rate of heat evolution is everywhere greater than that of heat transfer. Hence, the mixture is heated, the reaction is speeded up and ends with combustion. At a lower pressure  $P_1$  the mixture is first heated but only up to temperature  $T_1$  at which the heat evolution curve intersects with the heat-transfer straight line. The heating-up is stopped since the rates of heat evolution and heat transfer are equal and the chemical process is stationary. The pressure  $P_0$  at which the curves only touch each other is evidently the boundary, minimum pressure—ignition is possible only at  $P \equiv P_0$ . Such is the effect of pressure at a specified temperature of the wall.

Figure 9.9b shows the effect of the wall temperature at a given pressure  $P_0$ . The rise of the wall temperature leads to the decrease of the rate of heat transfer—to the shift of the straight line to the right. Thus, whereas at  $T_0^{(1)}$  thermal combustion is impossible, it will occur as the wall temperature increases, say, up to  $T_0^{(3)}$ .

Now we shall determine the relation between the minimum pressure  $P_0$  and the wall temperature. The combustion conditions are realized at the point of intersection, where the rates and their derivatives are equal, i.e.,

I. 
$$Qw_{(T_1)} = \varkappa \left(T_1 - T_0\right)$$
  
II.  $Q \left| \frac{dw}{dT} \right|_{(T=T_1)} = \varkappa$   $\right\}$  (9.27)

The reaction rate will be written provisionally in the following form:

$$w = Ce^{-E/RT} \tag{9.28}$$

which contains the quantity C defined as

$$C = \frac{Z_0}{(RT)^2} N_{\rm A} \left( 1 - N_{\rm A} \right) /$$
 (9.29)

which will be considered to be independent of temperature at a first approximation. Therefore,

$$\frac{dw}{dT} = \frac{CE}{RT^2} e^{-E/RT} \tag{9.30}$$

Hence, with account taken of Eqs. (9.28) and (9.30), the conditions (9.27) will assume the form:

I. 
$$QCe^{-E/RT_1} = \varkappa (T_1 - T_0)$$
II  $\frac{QCE}{RT_1^2} e^{-E/RT_1} = \varkappa$  (9.31)

From the second condition we determine the exponential function

$$e^{-E/RT_1} = \varkappa \frac{RT_1^2}{QCE}$$

and substitute into the first. We get

$$\frac{QC \kappa R T_1^2}{QCE} = \kappa \left( T_1 - T_0 \right)$$

10

$$\frac{R}{E}T_1^2 - T_1 + T_0 = 0 (9.32)$$

The physical significance is exhibited by the smaller root of this quadratic equation, i.e.,

$$T_{1} = \frac{1 - \sqrt{1 - 4\frac{RT_{0}}{E}}}{\frac{2R}{E}} \tag{9.33}$$

An approximate solution of the problem can be found by expanding the radical into Maclaurin's series, only the first two terms of the series being left. We obtain

$$\left(1 - \frac{4RT_0}{E}\right)^{1/2} \approx 1 - \frac{2RT_0}{E}$$

or, substituting the radical into Eq. (9.33),

$$T_1 \approx T_0$$
 (9.34)

Thus, we arrive at a somewhat unexpected result indicating the approximate equality of the wall temperature and the ignition temperature. In other words, thermal combustion may be almost isothermal at the very outset, which is accounted for by the strong dependence of the reaction rate on temperature and leads to the difficulties in the experimental determination of the nature of combustion.

The value of  $T_1 = T_0$  may be substituted into the second of the conditions (9.31):

$$\frac{QCE}{RT_0^2}e^{-E/RT_0} = \varkappa \tag{9.35}$$

and also C may be replaced by its expression from Eq. (9.29). We obtain the relation

$$\frac{DN_{\rm A} (1 - N_{\rm A}) P_0^2 E}{RT_0^2} e^{-E/RT_0} = \varkappa \tag{9.36}$$

in which the arbitrary pressure value has already been replaced by the pressure  $P_0$  which corresponds to the point of intersection.

We rewrite Eq. (9.36) in the following manner:

$$\frac{P_0^2}{T_0^2} = \left[\frac{\varkappa R}{DN_{\Lambda} (1 - N_{\Lambda}) E}\right] e^{E/RT} = C_0 e^{E/RT}$$
(9.37)

Here the quantity  $C_0$  designates the fraction in square brackets, which is only slightly dependent on temperature. Taking logarithms in Eq. (9.37)

$$\ln \frac{P_0}{T_0} = \frac{1}{2} \cdot \frac{E}{RT_0} + \frac{1}{2} \ln C_0$$

and introducing new constants, we finally get the relation\*

or 
$$\log \frac{P_0}{T_0} = \frac{A}{T_0} + B$$

$$\log P_0 = \log T_0 + \frac{A}{T} + B$$
(9.38)

which connects the minimum pressure of thermal combustion with the wall temperature.

Equation (9.38) and similar equations have been repeatedly tested and have been found satisfactory in general. Figure 9.10

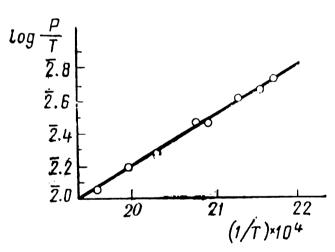


Fig. 9.10. The thermal combustion upon decomposition of Cl<sub>2</sub>O. Testing of formula (9.38) (after A. V. Zagulin).

gives, in appropriate coordinates, data on thermal combustion for the decomposition of chlorine oxide. The straight-line dependence of  $\log p/T$  on inverse temperature confirms the correctness of the form of the function (9.38).

In the cases discussed above, at pressures higher than  $P_0$  the combustion occurs without substantial delays: the induction period is short, less than 1 sec. In many cases, however, ignition takes place with much

greater delays. As an example may be cited the oxidation of methane by oxygen, where at  $t=730\,^{\circ}\text{C}$  and  $\rho=40\,\text{mm}$  Hg the induction period is close to 4 min. Long induction periods are also observed in the combustion of other hydrocarbons and also in the oxidation of carbon disulphide and hydrogen sulphide. In the combustion of solid and liquid explo-

<sup>\*</sup> Later, the authors reconsidered the derivation of the relation between  $P_0$  and  $T_0$  and obtained a somewhat different relation for a bimolecular reaction:  $(p_0/T_0^2) = A/T_0 + B$ . It however differs little from the relation given above.

sive substances, the induction periods that precede the combustion amount to several minutes and even hours. A more detailed study of the kinetics of these processes shows that they are of autocatalytic nature and the reaction velocity in the initial stage is described by the equation

$$w = \frac{dx}{dt} = n_0 + \varphi x \tag{9.39}$$

where x is the amount of substance reacted, and  $n_0$  is the number of molecules of the final product or of the intermediate in unit volume per unit time, which participate further in the reaction as catalytic centres. Integration of the equation gives the following result:

$$x = \frac{n_0}{\varphi} \left( e^{\varphi t} - 1 \right) \tag{9.40}$$

Substitution of x into the original differential equation yields the time dependence of the reaction velocity:

$$w = \frac{dx}{dt} = n_0 e^{\varphi t}$$

which does not differ functionally from formula (9.15), which was derived for the rate of a branching-chain reaction. Thus, the kinetics of autocatalytic thermal combustion may be similar outwardly to the kinetics of a pure chain combustion. All this must be taken into account in the study of reactions that end up with combustion or explosion.

### Kinetics of Photochemical Reactions in Gases

#### 10.1. Absorption of Light by a Homogeneous Medium

Since the time of Grotthus it has been known that a chemical change is produced only by the light absorbed. We shall consider now some laws of light absorption.

Let a parallel beam of monochromatic light of wavelength  $\lambda$  enter an infinitely thin (dx) layer of a homogeneous absorbing medium (Fig. 10.1). If I ergs fall on each square centimetre of the surface of the layer per second, we say that the light beam incident upon the layer is equal to I ergs/cm<sup>2</sup>·sec. Suppose that after having passed through a layer of thickness dx the light beam intensity diminished to I-dI, where dI is the radiant energy absorbed per second per 1 cm<sup>2</sup> of the layer.

Experiment shows that, first, each thin layer of constant thickness inside a homogeneous absorbing medium absorbs a definite proportion of the incident light beam. This law established by Bouguer in 1729 and by Lambert in 1760 is known as the Bouguer-Lambert law or, for short, as the Lambert law. The essence of the law is that the absorbing power of the medium is independent of the intensity of the incident light. The law is quite exact: Vavilov has found no deviations from this law; he conducted measurements within the range of variation of the light beam from  $10^{-11}$  to  $10^8$  erg/cm<sup>2</sup>·sec.

Second, according to experimental evidence, the absorption of light by a thin layer is proportional to the number of absorbing molecules contained in it, i.e., its concentration. This is **Beer's law** which was enunciated in 1852. It states that the **absorbing power of molecules is independent of the distance between them** and is an approximate law which is valid only at sufficiently low concentrations.

Let us write the mathematical formulations of these laws. The Bouguer-Lambert law may be stated as

$$-\frac{1}{I} \cdot \frac{dI}{dx} = K \tag{10.1}$$

But, according to Beer's law, the quantity K, which characterizes the absorbing power of the medium, is proportional to the concentration of absorbing molecules in the layer, n, i.e.,

$$K = kn \tag{10.2}$$

The thus introduced characteristic k is called the molecular absorption coefficient; it is no longer dependent \* on the concentra-

tion and is a measure of the absorbing power of molecules for a given wavelength. As can easily be seen from Eqs. (10.1) and (10.2), k has the dimensions of length squared  $(cm^2)$ .

Now we shall rewrite the combined law in the form

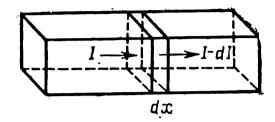


Fig. 10.1. The absorption of light by a substance.

$$-\frac{dl}{l} = kn \, dx \tag{10.3}$$

and integrate between the limits of x from 0 to l, where l is the total thickness of the absorbing layer, and of l from  $l_0$  to l.

Raising to a power yields

$$I = I_0 e^{-knl} \tag{10.4}$$

In this formulation the law is usually called the Lambert-Beer law. The radiant energy absorbed by a layer of cross-sectional area  $1~\rm cm^2$  and length l is given by

$$A = I_0 - I = I_0 (1 - e^{-knl})$$

In photochemistry, just as in chemistry in general, the concentration is more often expressed in moles per litre and not by the number of molecules in 1 cm<sup>3</sup>. In accordance with this, another constant is introduced, which characterizes the absorbing power of molecules for a light of a given wavelength, namely, the molar absorption coefficient; it is defined by the relation

$$kn = \varepsilon c$$

The relation between k and  $\epsilon$  is easily found:

$$\frac{k}{\varepsilon} = \frac{c}{n} = \frac{1000}{6.02 \times 10^{23}}$$

or  $k = 1.66 \times 10^{-21} \epsilon$ .

In practice, it is convenient to make use of the molar extinction coefficient  $\epsilon_{10}$ , with the Lambert-Beer law written in the form

$$I = I_0 \cdot 10^{-\epsilon_{10}cl} = I_0 e^{-2 \cdot 36.3 \cdot \epsilon_{10}cl}$$

from which it is obvious that

$$\varepsilon = 2.303 \cdot \varepsilon_{10}$$

<sup>\*</sup> To a first approximation.

Thus,

$$k = 1.66 \times 10^{-21} \epsilon = 3.82 \times 10^{-21} \cdot \epsilon_{10}$$

Such are the relations between all the absorption coefficients used in practice. For example, the value of  $\epsilon$  for coloured organic compounds is approximately equal to  $10^4$  at the absorption maximum. Hence, for the same substances

$$k = 10^4 \times 1.66 \times 10^{-21} = 1.66 \times 10^{-17} \text{ cm}^2$$

We shall return to the discussion of this value of k at a later time.

The Lambert-Beer law (10.3) may be represented also in the form

$$-\frac{dI}{I} = kdn \tag{10.5}$$

where  $dn = n \cdot dx$  will express the number of absorbing molecules in a layer of thickness dx and surface area 1 cm<sup>2</sup>. From relation (10.5) it follows that each molecule absorbs a definite proportion of light beam incident on the layer. In other words, the molecule behaves like a plane of surface area k cm<sup>2</sup> which is opaque to light of a given wavelength. As a rule, the dimensions of the plane are smaller than the size usually adopted for the molecules themselves. Thus, in the above-given example involving coloured organic compounds  $k \approx 2 \times 10^{-17}$  cm<sup>2</sup>. Assuming the diameter of the molecule to be equal to  $5 \times 10^{-8}$  cm, we obtain the cross-sectional area  $2 \times 10^{-15}$  cm<sup>2</sup>, i.e., the value which is 100 times greater.

Incidentally, the above interpretation of the molecular absorption coefficient allows one to obtain readily the Lambert-Beer law. A light beam of I ergs/cm<sup>2</sup>·sec corresponds to  $N_v = I/hv$  quanta/cm<sup>2</sup>·sec. On passing through a layer of thickness dx, which contains dn molecules, the number of photons diminishes by  $-dN_v$ . This decrease is equal to the product of the total number of photons incident upon 1 cm<sup>2</sup> per 1 sec,  $N_v$ , by the total surface area of opaque planes in the absorbing layer, which is equal to kdn, on the condition that separate molecules do not overlap one another, i.e., in a sufficiently dilute solution.

Thus,

$$-dN_{\mathbf{v}} = k \, dnN_{\mathbf{v}} = kn \, dxN_{\mathbf{v}}$$

or

$$-\frac{dN_{v}}{N_{v}} = -\frac{dI}{I} = kn \ dx$$

which is the usual formulation of the Lambert-Beer law in a differential form.

Thus, one of the factors responsible for the approximate nature of the Beer's law becomes clear, i.e., it is evident now that this law is applicable to sufficiently dilute solutions or gases of not too high a density.

#### 10.2. Basic Laws of Photochemistry

In 1817 Grotthus reported about his observation that a chemical change in matter can be produced only by light, the colouration of which is complementary to the colour of the material, i.e., the light absorbed by the material. In 1830 Draper gave a clearer formulation of essentially the same law: only light that is absorbed can be effective in producing a chemical change (the first law of photochemistry).

In 1904 van't Hoff formulated the quantitative regularity lying at the basis of the kinetics of photochemical reactions: the amount of a photochemically changed substance is proportional to the

radiant energy absorbed.

We may formulate this important law as follows. In time dt the concentration of a photochemically reacting substance changed by dc < 0, where c is the instantaneous concentration. On the other hand, if the photochemical system is a homogeneous absorbing layer of thickness l, the energy absorbed per second is given by

$$A = I_0 \left( 1 - e^{-\varepsilon cl} \right)$$

By the van't Hoff law,

$$-dc = \operatorname{const} \cdot A \cdot dt = \operatorname{const} \cdot I_0 \left( 1 - e^{-\varepsilon ct} \right) dt$$

or

$$-\frac{dc}{dt} = \operatorname{const} \cdot I_0 \left( 1 - e^{-\varepsilon cl} \right) \tag{10.6}$$

Expression (10.6) may be regarded as the mathematical formulation of the van't Hoff law. From this law we can draw the following conclusions. First, if the absorbing layer is thin, i.e., is equal to dx, the amount of energy absorbed per second is equal to

$$dA = I_0 \varepsilon c dx$$

Then

$$-\frac{dc}{dt} = (\operatorname{const} \cdot I_0 \varepsilon \, dx) \, c = k_1 c$$

and the reaction rate is proportional to the concentration of the reacting substance raised to a first power, i.e., the reaction is first order. Second, on the contrary, if *cl* is large (a thick absorbing layer, a large absorption coefficient), then

$$-\frac{dc}{dt} = \text{const} \cdot I_0$$

Now the entire light beam is absorbed, and the reaction rate is independent of the concentration (zero order) and is proportional to the light beam.

In 1912 Einstein published his famous law of photochemical equivalence. At present this law is formulated thus: each quantum ot light causes a change in one molecule (the second law of photochemistry).

In distinction to the original formulation by Einstein, in which it is stated that the light quantum absorbed causes a chemical conversion of a molecule, by the word change is now meant any change, both chemical and physical. The molecule may become excited when it absorbs light and then lose the excitation energy without having reacted.

Thus, the primary cause of a photochemical reaction is the absorption of light.

We now introduce the concept of the total quantum yield, or the quantum efficiency, of a process. This quantity is defined as

$$\gamma = \frac{\text{number of molecules decomposed or formed in the reaction}}{\text{number of quanta absorbed}}$$

For a discussion and interpretation of this most important photochemical quantity, the photochemical reaction should be divided into three principal, somewhat overlapping stages:

- (1) the initial act of light absorption;
- (2) the primary photochemical process;
- (3) secondary reactions.

We shall consider these stages separately, in the order in which they are listed above.

The Initial Absorption Act. The Grotthus-Draper law and the Einstein law formulate a necessary but insufficient condition for the initiation of a photochemical reaction. Thus, it may be noted that the light that causes the excitation of only the rotational and vibrational energy levels of the molecule is usually inactive photochemically. The corresponding infrared quanta are too small (their energy is tenths and hundredths of an electron-volt) to induce the rupture of bonds in the molecule.

The initial action of light in any gaseous photochemical reaction gives rise to an electronically excited molecule. The quantum yield of this process, i.e., the initial absorption act, is equal to unity in most cases. Since exceptions to this rule are rare, we assume it to be equal to unity without reservations.

The Primary Photochemical Process. Properly speaking, the primary photochemical process may include both the initial absorption act and the processes of conversion of an electronically excited molecule that follow immediately the absorption act. In general, if a molecule A absorbs a quantum of light, the following

possibilities of its primary conversion listed in Table 10.1 may be visualized.

Type of process Reaction equation I. Fluorescence  $A^* \rightarrow A + hv$  $A * + M \rightarrow A + M$ → II. Deactivation upon collision or at the wall → III. Direct spontaneous dis- $A^* \rightarrow D_1 + D_2$ sociation Initial act of ab-→ IV. Dissociation induced by sorption  $A^* + M \rightarrow D_1 + D_2 + M$ a collision  $A + hv = A^*$ V. Internal rearrangement  $A^* \rightarrow B$ or isomerization  $A * + B \rightarrow C$ VI. Reaction with other molecules

TABLE 10.1. Primary Processes Involving A\*

We may speak of the quantum yield of the primary photochemical process or, for short, of the primary quantum yield. Its definition is evidently associated with the nature of the process itself. If, for example, process VI, i.e., the reaction of an electronically excited molecule with another molecule, were the only one taking place, the primary quantum yield would coincide with the yield of the initial absorption act, i.e., would be equal to unity. Experimental data, however, indicate that only a few photochemical processes include a direct reaction of electronically excited molecules.

In the majority of photochemical reactions, however, the primary process leads to the dissociation of the absorbing molecule (process III). Thus, the primary quantum yield may be defined as follows:

$$\gamma_{l} = \frac{\text{number of molecules dissociating in the primary process}}{\text{number of quanta absorbed}}$$

Perhaps, the highest value of  $\gamma_I$  is unity, but if the other processes (most often, I and II) also take place,  $\gamma_I$  becomes smaller than unity. The value of  $\gamma_I$  is usually indeterminable by direct experiments. To find it, we must either obtain information about the total yield and the nature of the secondary processes or estimate the ratio of the rates of reactions I-V. The matters are often facilitated by the fact that not more than two or three of the processes listed are of importance and it becomes possible to evaluate, though approximately, the relative values of their rate constants.

A study of the absorption spectrum may be very helpful in this respect.

Figure 10.2 shows three types of potential-energy curves for diatomic molecules in their ground electronic state (the lower

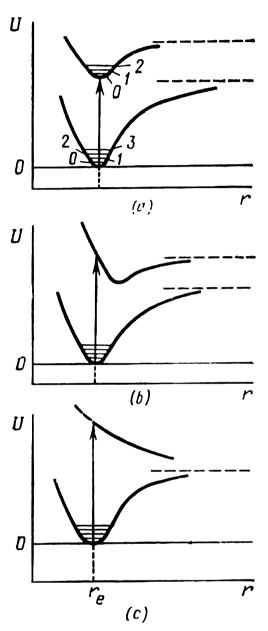


Fig. 10.2. Three types of electronic transitions upon absorption of light by a diatomic molecule:

(a)—no dissociation or dissociation is insignificant; (b)—dissociation is strong; (c)—each act of photon absorption is accompanied by dissociation.

curves with a low minimum) and in the electronically excited state (the upper curves). If the shape and relative positions of the potential-energy curves correspond to those shown in Fig. 10.2a, the absorption of light leads to a stable excited state in which the vibrational motion of atoms is possible. The absorption spectrum here is discrete, banded in accordance with the discrete energy The dissociation of molecules into atoms does not occur at all or occurs seldom when the light is absorbed the lower vibrational (marked by zero), which is the most probable at moderate temperatures, but at the higher excited levels.

The upper potential-energy curve in Fig. 10.2c has no minimum. This repulsive curve corresponds to the unstable excited state. Here, each absorption act leads to the dissociation of the molecule into atoms and the absorption spectrum is continuous since the dissociation product can carry away any amount of unquantized kinetic energy. A similar picture is observed, for example, when light is absorbed by the HF, HCl, HBr, HI and F<sub>2</sub> molecules.

In the intermediate case (Fig. 10.2b), the molecule upon absorption of light is found to be on the portion of the potential-energy curve that corresponds to the energy exceeding the dissociation energy. Here the light absorption most often also results in dissociation, and

the absorption spectrum is largely continuous. Thus, a continuous absorption spectrum indicates that the state A\* is unstable and the molecule dissociates rapidly. On continuous absorption the assumption that process III (Table 10.1) predominates over the others is probable. On the contrary, a discrete absorption spectrum points to the sluggishness of processes III and IV

(Table 10.1), because of which the other processes can compete with it.

Secondary Reactions. Let us divide the total quantum yield by the primary quantum yield. We get

$$\gamma_2 = \frac{\gamma}{\gamma_1} = \frac{\text{number of molecules decomposed or formed in reaction}}{\text{number of molecules dissociated in primary process}}$$

This ratio is a measure of the development of secondary reactions and may be termed the **secondary quantum yield.** Obviously,  $\gamma = \gamma_1 \gamma_2$ . The products of the primary dissociation,  $D_1$  and  $D_2$ , may be stable molecules, reactive molecules, or free radicals and atoms. If the dissociation products are stable molecules, then it is most likely that no subsequent reactions will occur, and the total yield will be equal to the primary yield and  $\gamma_2 = 1$ . But if the primary dissociation products are free radicals or atoms, as is most often the case, then secondary reactions may take place. In this case,  $\gamma_2$  may remain to be close to unity and deviate

TABLE 10.2. Secondary Reactions

	Type of process	Reaction equation*	Resultant value of γ <sub>2</sub>
VII.	Recombination	$D_1 + D_2 + M \rightarrow A + M$	<1
VIII.	Reaction with the product or any other molecules, involving the regeneration of A	$D_1 + B \rightarrow A + C$	<1
IX.	Non-chain reactions without participation of A and without formation of A	$ \begin{cases} D_1 + D_2 \rightarrow B + C \\ D_1 + D_2 \rightarrow B; D_2 + D_2 \rightarrow C \\ D_1 + B \rightarrow C, \text{ etc.} \end{cases} $	1
X.	Non-chain reactions involving new molecules A	$D_1 + A \rightarrow B + C$	2 or 3
XI.	Chain reactions without participation of molecules A	$ \begin{cases} D_1 + B \rightarrow E + D_2 \\ D_2 + C \rightarrow E + D_1 \end{cases} $	>1, possibly ≫1
XII.	Chain reactions with participation of molecules A	$ \begin{cases} D_1 + A \rightarrow B + D_2 \\ D_2 + A \rightarrow C + D_1 \end{cases} $	>1, possibly ≫1

<sup>\*</sup> B and C are stable molecules different from A.

strongly from it in both directions. In general, if molecule A dissociates into free radicals, the secondary reactions given in Table 10.2 are possible.

In accordance with the data presented in Table 10.2, a high quantum yield is indicative of the occurrence of secondary chain reactions. But if it is small, recombination VII or deactivation II may be suspected. If  $\gamma$  is equal to a small integer and depends but slightly on the conditions of the experiment (especially if the absorption spectrum is continuous), then, in all probability, there takes place a rapid and complete dissociation into stable molecules or radicals which react only according to Equations IX and X. Generally, the reaction mechanism can be deduced on the basis of a study of the dependence of  $\gamma$  on the conditions of the experiment, namely, (1) the concentrations or pressures of the reactants and also of the inert substances added; (2) light intensity (the light beam intensity); (3) wavelength; (4) temperature; (5) the size of the vessel and the wall material.

#### 10.3. Determination of the Primary Quantum Yield

Let us return to primary processes and the primary quantum yield, which govern the subsequent course of the reaction. Table 10.1 lists 6 possible primary photochemical processes. In kinetic studies, however, resort is made to simplifying assumptions. Namely, based on some preliminary data, we choose the most important primary processes, neglecting the others. Having obtained further, on the basis of the assumptions made, the mathematical relations, we compare them with the experimental data. Such simplifying assumptions include the so-called Stern-Volmer mechanism which is frequently employed in practical investigations.

Suppose that the primary absorption of light is accompanied by fluorescence, the intensity of which can be measured. Besides, the molecule that has primarily absorbed light can be deactivated upon collision with another starting molecule A and can also dissociate. In other words, let us assume that the initial absorption act is followed by three primary processes only. We are to determine the primary quantum yield under the conditions indicated above.

Thus, according to Stern and Volmer, the following mechanism is thought to occur:

Absorption 
$$A + hv \longrightarrow A^*$$
Primary processes:

1. Fluorescence  $A^* \longrightarrow A + hv$ 
 $k_1 = \frac{1}{\tau}$ 
2. Deactivation  $A^* + A \longrightarrow A + A$ 
3. Dissociation  $A^* \longrightarrow D_1 + D_2$ 
 $k_3$ 

In estimating the absorption  $I_a$  is the intensity of the light absorbed equal to the rate of formation of the excited state.\* The rate of dissociation may evidently be written thus

$$\frac{d[D_1]}{dt} = \frac{d[D_2]}{dt} = k_3 [A^*]$$
 (10.8)

To replace the concentration of  $A^*$ , which is usually not directly determinable, use is made of the steady-state approximation (see Sec. 3.4) by applying it to the unstable intermediate  $A^*$ ;

$$I_a = k_1 [A^*] + k_2 [A^*] [A] + k_3 [A^*]$$

Hence

$$[A^*] = \frac{I_a}{k_1 + k_2 [A] + k_3}$$

Substituting the value of  $[A^*]$  found into Eq. (10.8), we obtain the rate of dissociation of A:

$$\frac{d [D_1]}{dt} = \frac{I_a}{1 + \frac{k_1 + k_2 [A]}{k_3}}$$

The primary quantum yield is equal to the ratio of the rate of dissociation to the rate of light absorption, i.e.,

$$\gamma_1 = \frac{1}{I_a} \cdot \frac{d \left[ D_1 \right]}{dt} = \frac{1}{1 + \frac{k_1 + k_2 \left[ A \right]}{k_3}}$$
 (10.9)

Let us now turn our attention to fluorescence which, as we have said, can be changed. Let the number of fluorescence quanta emitted per 1 cm<sup>3</sup> per second be equal to  $I_f = k_1[A^*]$ . The quantity  $I_a$  is, as before, the intensity of the light absorbed. Then, if the steady-state conditions are applicable to the volume under consideration, we may write

$$I_a = I_f + k_2 [A^*] [A] + k_3 [A^*]$$

or

$$I_a - I_l = k_2 [A^*] [A] + k_3 [A^*]$$

Dividing the last expression by  $I_f = k_1[A^*]$ , we obtain

$$\frac{I_a}{I_f} = 1 + \frac{k_3 + k_2 [A]}{k_1} = 1 + \frac{k_3}{k_1} + \frac{k_2}{k_1} [A]$$
 (10.10)

The ratio of the number of absorbed quanta to the number of quanta emitted by way of fluorescence is a measure of fluorescence quenching. If the dependence of fluorescence quenching on the concentration of the absorbing substance [A] is measured, then, by

<sup>\*</sup> As has already been pointed out, the quantum yield of the absorption act is assumed to be equal to unity;  $I_a$  is expressed in quanta/cm<sup>3</sup>·sec or in einsteins (moles of quanta)/cm<sup>3</sup>·sec.

Eq. (10.10), the graphical representation of this dependence must be expressed by a straight line (Fig. 10.3). The slope of the straight line tan  $\alpha = k_2/k_1$ , and the intercept on the ordinate  $a = 1 + k_3/k_1$ . Thus, the Stern-Volmer mechanism leads to a linear dependence of the quenching on the concentration, which allows one to find the ratios of the constants,  $k_2/k_1$  and  $k_1/k_3$ ,

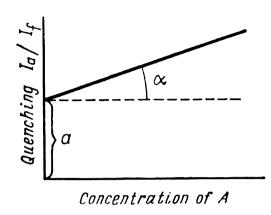


Fig. 10.3. The dependence of fluorescence quenching on the concentration of the absorbing substance (for the determination of the primary quantum yield).

and, hence, the ratio  $k_2/k_3$ . The ratio found can be substituted into Eq. (10.9) and the primary quantum yield determined. The procedure actually used in practice is somewhat more complicated than the one described above since corrections for the absorption occurring on the way to the measuring instrument must be introduced into the fluorescence measured. We shall not dwell on the details involved; we shall only indicate that the observation of the straight-line dependence of the form shown in Fig. 10.3 is regarded as a proof of the Stern-Volmer mechanism, i.e., a mechanism in which the destruc-

tion of excited molecules by way of a bimolecular deactivation competes with the unimolecular fluorescence. Such is one of the possibilities of determination of the primary quantum yield. We shall not dwell on the other possibilities, referring the reader to special publications.

# 10.4. Some Kinetic Equations of Photochemical Reactions Without Participation of Chains

We shall now be concerned with the consideration of secondary reactions. Suppose a molecule A absorbs light and dissociates with a primary quantum yield  $\gamma_l$ . Let us assume further the following possibilities: one of the dissociation products can react either with molecule A or with one of the end products. The other dissociation product undergoes recombination. No chain is generated. The overall reaction may be written in the form

$$2A \longrightarrow B + C$$

This may be exemplified by the decomposition of HBr or HI. The mechanism may be represented in the following form:

(1) 
$$A + hv \longrightarrow D_1 + D_2$$
  $\gamma_1 I_a$   
(2)  $D_1 + A \longrightarrow B + D_2$   $k_2$   
(3)  $D_1 + C \longrightarrow A + D_2$   $k_3$   
(4)  $D_2 + D_2 + M \longrightarrow C + M$   $k_4$ 

Or, when applied to HBr:

$$HBr + hv \longrightarrow H + Br$$
 $H + HBr \longrightarrow H_2 + Br$ 
 $H + Br_2 \longrightarrow HBr + Br$ 
 $Br + Br + M \longrightarrow Br_2 + M$ 

Referring to the reaction in the general form, we shall assume that the rates of formation of end products, say B, can be determined experimentally. We can write further:

$$\frac{d[B]}{dt} = k_2[D_1][A] \tag{10.11}$$

On the other hand, the application of the steady-state method to the dissociation product  $D_1$  gives the equation

 $\gamma_1 I_a = k_2 [D_1] [A] + k_3 [D_1] [C]$ 

or

$$D_1 = \frac{\gamma_1 I_a}{k_2 [A] + k_3 [C]}$$
 (10.12)

Substituting  $[D_1]$  into the equation for the observed velocity (10.11), we obtain

$$\frac{d[B]}{dt} = \frac{k_2 \gamma_1 I_a[A]}{k_2[A] + k_3[C]} = \frac{\gamma_1 I_a}{1 + \frac{k_3}{k_2} \cdot \frac{[C]}{[A]}}$$

The total quantum yield of the reaction with respect to product B is equal to

$$\gamma_{\rm B} = \frac{1}{I_a} \cdot \frac{d \, [{\rm B}]}{dt} = \frac{\gamma_1}{1 + \frac{k_3}{k_2} \cdot [{\rm C}]}$$
(10.13)

At the start of the reaction the concentration of the product [C] = 0. Therefore, in the initial period  $\gamma_B = \gamma_1$  or  $\gamma_A = 2\gamma_1$ . As the products accumulate (or C is added) the total quantum yield will diminish, tending to zero.

Taking the inverse of the total yield (10.13)

$$\frac{1}{\gamma_{\rm B}} = \frac{1}{\gamma_{\rm I}} + \frac{k_3}{k_2 \gamma_{\rm I}} \cdot \frac{[C]}{[A]} \tag{10.14}$$

we see that it must be a linear function of the ratio of the concentrations, [C]/[A]. Specifying the various compositions of the original mixture, i.e., [C]/[A], and determining  $\gamma_B$  for them, we can, by constructing a corresponding straight line, find the ratio  $k_3/k_2\gamma_1$  from the slope of the straight line and the ratio  $1/\gamma_1$  from the intercept on the ordinate.

Hence, the method just described enables one to find the primary quantum yield as well and the relative value of the rate constants for elementary reactions 2 and 3.

Further information can be obtained by carrying out an investigation at different temperatures. Suppose the dependence  $\gamma_B = f([C]/[A])$  is known for a number of temperatures. Then, for the same temperatures we know the ratio  $k_3/k_2$ . But, using the Arrhenius equation, we can write

$$k_2 = A_2 e^{-E_2/RT}$$
 and  $k_3 = A_3 e^{E_3/RT}$ 

or

$$\frac{k_3}{k_2} = \frac{A_3}{A_2} e^{\frac{E_2 - E_3}{RT}}$$

and

$$\log \frac{k_3}{k_2} = \log \frac{A_3}{A_2} + \frac{E_2 - E_3}{2.3RT}$$

Evidently, the plotting of a straight line in the coordinates  $\log (k_3/k_2)$  and f(1/T) will also give the ratio of the pre-exponential factors  $A_3/A_2$  and the activation difference  $E_2 - E_3$ . The separate values of these quantities cannot however be determined in this way.

The most reliable method of determining the separate values of  $k_2$  and  $k_3$ , i. e., in the particular cases of the reactions

$$H + HBr \longrightarrow H_2 + Br \qquad k_2$$

and

$$H + Br_2 \longrightarrow HBr + Br$$
  $k_3$ 

would be the study of each of these elementary reactions separately. For hydrogen atoms this is not very difficult and it has in fact been done, but in general such a possibility is offered not very often.

In other isolated cases the information on  $k_2$  and  $k_3$  can be gleaned indirectly by the method of parallel reactions. Suppose that the primary dissociation product  $D_1$  can also be subjected to the reaction

$$(5) D_1 + E \longrightarrow F + G \qquad k_5$$

the rate constant and activation energy of which are known. As soon as substance E is introduced into the reaction vessel the reaction 5 begins to compete with reactions 2 and 3 as to the consumption of  $D_1$ , and the equation for the quantum yield with respect to B will be written thus:

$$\gamma_{\mathrm{B}}' = \frac{\gamma_{1}}{1 + \frac{k_{3}}{k_{2}} \cdot \frac{[\mathsf{C}]}{[\mathsf{A}]} + \frac{k_{5}}{k_{2}} \cdot \frac{[\mathsf{E}]}{[\mathsf{A}]}}$$

Combining this relation and Eq. (10.13), we obtain

$$\gamma_1 \left( \frac{1}{\gamma_B'} - \frac{1}{\gamma_B} \right) = \frac{k_5}{k_2} \cdot \frac{[E]}{[A]}$$

Determination of the quantum yields in the presence and in the absence of E makes it possible to determine  $k_2$  and, hence,  $k_3$ .

# 10.5. Some Kinetic Equations of Photochemical Reactions Involving Chains

Let us now examine some typical secondary reactions involving chains. Suppose a molecule A absorbs light and dissociates with a primary yield  $\gamma_l$  into two identical parts. The secondary reactions that follow the dissociation involve chains which are terminated by way of destruction of the chain carriers on the walls at low pressures and by way of a homogeneous recombination involving a third body at high pressures. The overall reaction caused by the chain is as follows:

$$A + B \longrightarrow 2C$$

As examples of such reactions may be cited the various reactions of chlorination and, in general, of halogenation. Let substance A be chlorine. The mechanism of the reaction may be represented in the form:

Primary process (1) 
$$A + hv \longrightarrow D_1 + D_1 \qquad \gamma_1 I_a$$
 chain  $\begin{cases} (2) D_1 + B \longrightarrow C + D_2 & k_2 \\ (3) D_2 + A \longrightarrow C + D_1 & k_3 \end{cases}$  Chain termination 
$$\begin{cases} \text{low pressures} \\ (\text{at the wall}) \end{cases} \begin{cases} (4) D_1 + S \longrightarrow \frac{1}{2} A \dots & k_4 \\ (5) D_2 + S \longrightarrow X \dots & k_5 \\ (\text{in the bulk}) \end{cases} \begin{cases} (6) D_1 + D_1 + M \longrightarrow A + M & k_5 \\ (7) D_2 + D_2 + M \longrightarrow Y + M & k_7 \end{cases}$$

Generally speaking, the rate law can be derived by proceeding from all the seven elementary processes listed above. This path is however not fruitful because of the great complexity of the relations obtained. It is expedient to consider four limiting cases where one of the chain termination reactions, 4, 5, 6 or 7, is predominating. Independently of the nature of chain termination, the rate of formation of substance C is given by the equation

$$\frac{d[C]}{dt} = k_2[D_1][B] + k_3[D_2][A]$$

We shall further make certain assumptions.

I. Chains are terminated only by way of destruction of  $D_1$  on the wall. This condition can approximately be realized at low pressures if reaction 3 is sufficiently fast as compared with the other paths of disappearance of  $D_2$ .

Applying the steady-state principle to D<sub>1</sub> and D<sub>2</sub>, we find

$$2\gamma_1 I_a + k_3 [D_2] [A] = k_2 [D_1] [B] + k_4 (S) [D_1]$$
  
 $k_2 [D_1] [B] = k_3 [D_2] [A]$ 

Summing up both equations, we obtain

$$[D_1] = \frac{2\gamma_1 I_a}{k_4(S)}$$

and substitute it into the rate law

$$\frac{d[C]}{dt} = k_2[D_1][B] + k_3[D_2][A] = 2k_2[D_1][B] = \frac{4k_2\gamma_1/a[B]}{k_4(S)}$$
(10.15)

And the total quantum yield with respect to substance C is found by dividing Eq. (10.15) by the intensity of the light absorbed  $(I_a)$ :

$$\gamma_{\rm C} = \frac{1}{I_a} \cdot \frac{d [{\rm C}]}{dt} = \frac{4k_2 \gamma_1 [{\rm B}]}{k_4 (S)}$$
 (10.16)

So, the result is the equation for the reaction which is first order in B. The velocity does not depend explicitly on the concentration of A (at constant intensity of the light absorbed  $I_a$ ). The factor (S) in the equations obtained is a function of the wall activity, the rate of diffusion, and the convection involved. In general, (S) diminishes with increasing pressure. The proportionality of the velocity to the quantity  $k_2$ [B] is consistent with the assumption that  $k_3$  is large and therefore reaction 2 is a rate-determining step.

II. Chains are terminated only by way of destruction of  $D_2$  on the wall (process 5). The approach to the realization of this condition is possible at low pressures when reaction 2 is much faster than the other paths of disappearance of  $D_1$ .

We apply the steady-state principle to  $D_1$  and  $D_2$ :

$$2\gamma_1 I_a + k_3 [D_2] [A] = k_2 [D_1] [B]$$
  
 $k_2 [D_1] [B] = k_5 [D_2] (S)$ 

or

$$[D_2] = \frac{2\gamma_1 I_a}{k_5 (S)}$$

The rate of accumulation of the end product is written thus:

$$\frac{d[C]}{dt} = k_2[D_1][B] + k_3[D_2][A] = 2\gamma_1 I_a + 2k_3[D_2][A] = 2\gamma_1 I_a + \frac{4k_3\gamma_1 I_a[A]}{k_5(S)}$$
(10.17)

Obviously the total quantum yield with respect to C will be expressed by the equation

 $\gamma_{\mathfrak{C}} = 2\gamma_1 + \frac{4k_2\gamma_1 [A]}{k_{\mathfrak{C}}(S)}$ (10.18)

As seen from relation (10.18), the total yield approaches  $2\gamma_1$  as [A] is decreased, whereas in the first case [see relation (10.16)] the total yield  $\gamma_C$  tends to zero with decreasing [B]. This difference must be understandable—in this particular case the two primarily formed particles  $D_1$  react with B, giving two molecules C. At small concentrations of A the chains do not develop all particles D<sub>2</sub> are destroyed. At large [A] the possibility may arise that  $D_2$  may react with A, regenerating  $D_1$ —the chain development begins and the quantum yield increases. But in the first variant, at small [B], all the particles D1 are destroyed and  $\gamma_{\rm C}$  tends to zero.

III. Chains are terminated only by way of homogeneous recombination 6:

$$D_1 + D_1 + M \longrightarrow A + M$$

Such a predomination of process 6 may probably take place at high pressures and with a high rate of reaction 3 as compared with reactions 2 and 7.

As before, we apply the steady-state principle to  $D_1$  and  $D_2$ :

$$2\gamma_1 I_a + k_3 [D_2] [A] = k_2 [D_1] [B] + 2k_6 [D_1]^2 [M]$$

and

$$k_2[D_1|[B] = k_3[D_2][A]$$

from which

$$[D_1] = \left(\frac{\gamma_1 I_a}{k_6 [M]}\right)^{1/2}$$

and the observed reaction rate

$$\frac{d[C]}{dt} = k_2[D_1][B] + k_3[D_2][A] = 2k_2[D_1][B]$$

or

$$\frac{d[C]}{dt} = \frac{2k_2 \gamma_1^{1/2} I_a^{1/2} [B]}{k_6^{1/2} [M]^{1/2}}$$

and the quantum yield

$$\frac{d [C]}{dt} = \frac{2k_2 \gamma_1^{1/2} I_a^{1/2} [B]}{k_6^{1/2} [M]^{1/2}}$$
ield
$$\gamma_C = \frac{2k_2 \gamma_1^{1/2} [B]}{k_6^{1/2} [M]^{1/2} I_a^{1/2}}$$
(10.19)

IV. Chains are terminated only by way of homogeneous recombination 7:

$$D_2 + D_2 + M \longrightarrow Y + M$$

This can be realized at high pressures and if the rate of reaction 2 is great as compared with reactions 3 and 6.

Performing manipulations like those done repeatedly, we find

the reaction rate:

$$\frac{d[C]}{dt} = 2\gamma_1 I_a + \frac{2k_3 \gamma_1^{1/2} I_a^{1/2} [A]}{k_7^{1/2} [M]^{1/2}}$$

and the quantum yield

$$\gamma_{\rm C} = 2\gamma_1 + \frac{2k_3\gamma_1^{1/2} [A]}{k_7^{1/2} [M]^{1/2} I_a^{1/2}}$$
(10.20)

A rather substantial difference between relations (10.15) and (10.17) for the chain termination on the wall, on the one hand, and expressions (10.19) and (10.20) for the chain termination in the bulk, on the other, is the presence in the latter two expressions of a square root of the intensity of the light absorbed  $I_a$ . This difference in the dependence of the reaction rate and  $\gamma$  on  $I_a$  may serve as one of the direct and significant indications of the nature of the developing photochemical reaction. Namely, if the reaction rate is proportional or the total quantum yield is inversely proportional to the square root of the intensity of the light absorbed, then an important part in the mechanism is played by the recombination process which is second order with respect to the corresponding atoms or radicals. We may even state that in this case the principal (and practically the only) process of destruction of atoms or radicals is the recombination in the bulk. On the other hand, if the reaction rate is proportional to the intensity of the light absorbed, and the total quantum yield does not depend on it, such a recombination does not play a significant role and the disappearance of the chain carrier occurs, most probably, by first-order kinetics, i.e., on the wall.

Returning once again to the expressions for quantum yields, we note the following: in cases II and IV the construction of a plot of  $\gamma_C$  versus the concentration of reactant A and the extrapolation to  $[A] \rightarrow 0$  lead directly to the primary quantum yield  $\gamma_1$ . In cases I and III, the yield  $\gamma_1$  is indeterminable without additional data.

Let us consider one more problem. Since this section is concerned with secondary reactions involving chains, it is expedient to return once more to the concept of the average chain length v. It is timely especially as the determination of v from photochemical evidence is perhaps the most reliable. In application to the mechanism under discussion we shall define the chain length as the average number of cycles of reactions of the type

(2) 
$$D_1 + B \longrightarrow C + D_2$$
  $k_2$   
(3)  $D_2 + A \longrightarrow C + D_1$   $k_3$  2 cycles

per primary radical  $D_1$ . Since each cycle gives a molecule of product C, then the average number of cycles per  $1 \text{ cm}^3$  per 1 sec is equal to the rate of the observed reaction, dc/dt. But the average number of radicals  $D_1$  formed primarily in the same volume per unit time equals  $2\gamma_1 I_a$ . In general, the average chain length

$$v = \frac{1}{2\gamma_1 I_a} \cdot \frac{d[C]}{dt} = \frac{\gamma_C}{2\gamma_1}$$
 (10.21)

For the limiting cases considered above we have:

As can be seen, in cases I and III, as [B] decreases the chain length tends to zero—the probability of reaction 2 decreases and the probability of disappearance of  $D_1$  increases. In cases II and IV, with decrease of the concentration [A] the chain length tends to unity—the probability of regeneration of  $D_1$  by reaction 3 is reduced and the probability of disappearance of  $D_2$  is increased.

#### 10.6. The Dark Reaction

If a photochemical reaction is accompanied by a thermal or "dark" reaction, then at temperatures when the dark reaction is noticeable it is usually impossible to observe the photochemical reaction alone. In this case, one determines the rates of the overall reaction and the dark reaction separately. Ordinarily, the rate of the dark reaction is simply subtracted from the overall rate and the difference is considered to be equal to the rate of the photochemical reaction. This procedure, however, is not always justified and may lead to erroneous results. As an example, suppose that the mechanism of the photochemical reaction is analogous to the limiting case III (of those discussed in the preceding section), i.e., in the primary act the molecule A absorbs light and dissociates into two identical radicals D<sub>1</sub>. The radicals initiate a chain which is terminated only by the homogeneous recombination of D<sub>1</sub>. We shall now assume additionally the probability of

the thermal dissociation of molecules A into the same two radicals  $D_1$ . On the whole, the mechanism will have the form

(1) 
$$A + hv \longrightarrow D_1 + D_1$$
  $\gamma_1 I_a$  Additional (1a)  $A + M \longrightarrow D_1 + D_1 + M$   $k_1$  thermal (2)  $D_1 + B \longrightarrow C + D_2$   $k_2$  process (3)  $D_2 + A \longrightarrow C + D_1$   $k_3$  (6)  $D_1 + D_1 + M \longrightarrow A + M$   $k_6$ 

Applying the steady-state approximation to  $D_2$ , we obtain

$$k_2[D_1][B] = k_3[D_2][A]$$

We now write the overall (measurable) rate of the reaction

$$\frac{d[C]}{dt} = k_2[D_1][B] + k_3[D_2][A] = 2k_2[D_1][B]$$

This equation has already been encountered in the discussion of the mechanism III; the reaction rate is determined by the concentration of  $D_1$ .

Now we first imagine that only a dark reaction takes place. Then the steady-state concentration of  $D_1$  is determined from the relation

$$2k_1 [A] [M] + k_3 [D_2] [A] = k_2 [D_1] [B] + 2k_6 [D_1]^2 [M]$$

which, with the steady-state principle applied to D2, gives

$$[D_1] = \left\{ \frac{k_1 [A]}{k_6} \right\}^{1/2}$$

Thus, the measurable reaction rate \* is given by

$$\left(\frac{d\left[C\right]}{dt}\right)_{\text{dark}} = 2k_2 \left(\frac{k_1\left[A\right]}{k_6}\right)^{1/2} \left[B\right] \tag{10.22}$$

If only a photochemical reaction occurs (this variant was discussed in detail in Sec. 10.5), the steady-state concentration is determined by the relation

$$[D_1] = \left(\frac{\gamma_1 I_a}{k_6 [M]}\right)^{1/2}$$

and, hence, the rate is given by

$$\left(\frac{d\left[C\right]}{dt}\right)_{\text{ph}} = 2k_2 \left(\frac{\gamma_1 I_a}{k_6 \left[M\right]}\right)^{1/2} \left[B\right]$$
 (10.23)

What is of more interest to us now is the simultaneous occurrence of a photochemical and a dark reaction. Taking into account all the mechanisms given above, we find from the steady-state con-

<sup>\*</sup> Incidentally, a fractional half-order of the reaction appears here with respect to substance A.

dition for [D<sub>1</sub>]:

$$2\gamma_1 I_a + 2k_1 [A] [M] + k_3 [D_2] [A] = k_2 [D_1] [B] + 2k_6 [D_1]^2 [M]$$

whence

$$[D_1] = \left(\frac{k_1 [A]}{k_6} + \frac{\gamma_1 I_a}{k_6 [M]}\right)^{1/2}$$

and the overall measurable velocity is

$$\left(\frac{d[C]}{dt}\right)_{\text{overall}} = 2k_2 \left\{ \frac{k_1[A]}{k_6} + \frac{\gamma_1 l_a}{k_6[M]} \right\}^{1/2} [B]$$
 (10.24)

Obviously, by simply subtracting the rate of the dark reaction (10.22) from the overall rate (10.24) we shall not obtain the rate of the photochemical reaction (10.23). To find the latter, we must in this case subtract the square of the rate of the dark reaction from the square of the overall rate and then extract a square root from the difference, i.e.,

$$\left(\frac{d\left[C\right]}{dt}\right)_{\text{ph}} = \left\{\left(\frac{d\left[C\right]}{dt}\right)_{\text{overall}}^{2} - \left(\frac{d\left[C\right]}{dt}\right)_{\text{dark}}^{2}\right\}^{1/2} = 2k_{2}\left(\frac{\gamma_{1}I_{a}}{k_{6}\left[M\right]}\right)^{1/2}\left[B\right]$$

In general, it may be stated that if the photochemical and dark reactions proceed by quite independent routes, the overall rate will be the sum of the two rates taken separately. A simple subtraction will then be permissible. But if the mechanisms of the light and dark reactions involve at least one common secondary process, the overall rate will depend on the manner in which the concentration of particles that determine the rate depends on the light intensity and reactant concentration. Using the examples that have been given earlier, it can be shown that under the conditions of direct proportionality (say,  $[D_1] \approx I_a$ ) the overall velocity will really be the sum of the rates of the photochemical and dark reactions. But if [D<sub>1</sub>] is proportional to the square root of light intensity (upon chain termination in the bulk) or of the reactant concentration, then the overall rate will be equal to the square root of the sum of the squares of the rates of the photochemical and dark reactions.

## 10.7. Some Simple Photochemical Gas Reactions

Passing over now to the consideration of concrete photochemical reactions, we shall choose the following two simplest classes out of the vast variety of reactions that have been studied up to now for a more detailed study:

- I. Reactions which result from the absorption of light by atoms.
- II. Reactions which result from the absorption of light by diatomic molecules.

We shall begin with the first class in which we include reactions with electronically excited atoms and reactions initiated by such atoms.

Let us examine the possible conversions of an atom of a gaseous substance exposed to light.

The process of light absorption is

$$(1) X + hv \longrightarrow X^*$$

where X\* is an atom being on a higher electronic energy level. The electronically excited atom may undergo the following conversions:

(2) 
$$X^* \longrightarrow X + hv$$
 (fluorescence)

The spontaneous emission from excited states, with which fluorescence is associated, is kinetically described by a first-order equation.

Table 10.3 gives the average lifetimes (i.e., the inverse of the intensity of the emission of radiation) of some excited states of various atoms.

TABLE 10.3. The Average Lisetimes of Some Electronically Excited Atoms

Atom	Tran	sition	Wavelength of radiation, Å	$\tau = \frac{1}{k_{\rm I}}$ , sec
He	$2^{1}P_{1}$	$1^{1}S_{0}$	584	$4.4 \times 10^{-10}$
Н	$2^2P$	$1^2S_{1/2}$	1216	$1.2 \times 10^{-8}$
Li	$2^2P$	$2^{2}S_{1/2}$	6708	$2.7 \times 10^{-8}$
Na	$3^2P$	$2^{3}S_{1/2}^{72}$	5896	$1.6 \times 10^{-8}$
K	$4^{2}P$	$4^2S_{1/2}^{7}$	7699	$2.7 \times 10^{-8}$
Cs	$6^2P_{1/2}$	$6^2S_{1/2}^{7/2}$	8944	$3.8 \times 10^{-8}$
Cs	$6^2 P_{3/2}^{2}$	$6^{-1}S_{1/2}$	8521	$3.3 \times 10^{-8}$
Mg	$3^3P_1^{\prime\prime}$	$3^{1}S_{0}$	4571	$4.0 \times 10^{-3}$
Zn	$4^{3}P_{1}$	$4^{1}S_{0}$	3076	$1.0 \times 10^{-5}$
Cd	$5^{3}P_{1}$	$5^{1}S_{0}$	3261	$2.4 \times 10^{-6}$
Cd	$5^{!}P_{1}$	$5^{1}S_{0}$	2288	$2.0 \times 10^{-9}$
Hg	$6^3P_1^0$	$6^{1}S_{0}$	2537	$1.1 \times 10^{-7}$
Hg	$6^{1}P_{1}$	$6^{1}S_{0}$	1849	$1.3 \times 10^{-9}$
Hg	$6^3P_0^0$	$6^{1}S_{0}$	2656	ca. $10^{-3}$

In general, it may be said that usually  $\tau=1/k_1$  is a value of the order of  $10^{-7}$  to  $10^{-8}$  sec. Some states (Hg,  $6^3P_0^0$ , in Table 10.3), however, can radiate only by way of so-called "forbidden" transitions. The average lifetimes of such states are rela-

tively very long ( $10^{-3}$  to  $10^{-4}$  sec) and are called metastable states. Since the average time between molecular collisions under standard conditions (1 atm, 298 K) is approximately equal to  $10^{-10}$  sec (Sec. 6.3), the metastable state has little chance to lose energy by way of radiation and a much greater chance to undergo deactivation:

(3) 
$$X^* + M \longrightarrow X + M$$
 (deactivation)

In the last case it is believed that the electronic excitation energy is transformed into the translational, rotational, or vibrational energy of colliding particles. In processes 2 and 3, no chemical change takes place:

$$(4) X^* + AB \longrightarrow A + B + X$$

In this process, the molecule AB dissociates, and the atom X reverts to the ground state. The excess energy (the difference between the excitation energy of the atom and the dissociation energy of the molecules) is transformed into the translational, vibrational, or rotational energy:

$$(5) X^* + M \longrightarrow X' + M$$

In such a process, the atom  $X^*$  undergoes a change to assume a state which differs from the initial excited state  $X^*$ . The state X' may be energetically either lower or higher. The difference in energy between the two states turns into one of the ordinary forms or is taken from them during collision:

(6) 
$$X^* + AB \longrightarrow XA + B$$

that is, the atom X\* unites with one of the particles of the molecule, the other being released. The entity XA may prove stable in some cases and dissociate in others. The thus formed particles A and B can enter further reactions:

$$(7) X^* + A \longrightarrow A' + X$$

What is meant here is the transformation of the electronic excitation energy of X\* into any other kind of energy of the molecule A'. Collisions associated with such energy transformations are termed collisions of the second kind. Processes 3 and 4 belong to this category. In general, a collision of the first kind is accompanied by conversions of kinetic (or any other) energy into the electronic excitation energy. For example,

$$X + e \longrightarrow X^* + e$$
 (collision of the first kind)

On the contrary, on collision of the second kind

$$X^* + e \longrightarrow X + e$$
 (collision of the second kind) \*

<sup>\*</sup> For the role played by collisions of the second kind in reactions taking place in electrical discharges, see Chapter 11.

the energy of electronic excitation is transformed into kinetic energy, either vibrational or rotational.

In process 7 the molecule or atom A is raised to a higher energy level and  $X^*$  returns to the ground state (or, in general,

to a lower energy level).

The first indications of the possibility of the occurrence of some of these processes were obtained in 1922 by Cario and also by Cario and Franck.

Cario established that upon illumination of a mixture of mercury and thallium vapours by light of 2537.5 Å emitted by a mercury-vapour lamp the fluorescence composition shows a series of thallium lines. But if gaseous thallium alone is illuminated by the same light, no fluorescence takes place. An explanation was provided by studying a process of type 7. Radiation of 2537.5 Å is first absorbed by mercury atoms:

$$\operatorname{Hg}({}^{1}S_{0}) + hv \longrightarrow \operatorname{Hg}^{*}({}^{3}P_{1}^{0})$$

with the formation of an excited state with an energy corresponding to  $112.6 \text{ kcal/g} \cdot \text{atm}$  (39409.6 cm<sup>-1</sup>).

This is followed by

$$Hg^* + Tl \longrightarrow Hg + Tl'$$
  
 $Tl' \longrightarrow Tl + hv$ 

The symbol Tl' is used here to denote states with different degrees of excitation, which does not exceed the energy of the excited mercury atom.

Some important experiments were carried out by Cario and Franck. They demonstrated that in the mixture of mercury vapour and hydrogen illuminated by a mercury line of 2537.5 Å there appears a modification of hydrogen possessing enhanced chemical activity, which is capable of recovering oxides of metals.

Since the explosion energy of the bond of the hydrogen mole-

$$H_2 \longrightarrow H + H$$

is approximately equal to 4.55 electron-volts and the excitation energy of the mercury atom in its  $6^3P_1^0$  state is 4.86 electron-volts, this energy is more than enough for the dissociation of the hydrogen molecule into the atoms. Indeed, at a later time (Sent-fleben, 1925) the measurement of the heat conductivity of the illuminated mixture showed the presence in it of hydrogen atoms. Thus, the appearance of atoms is beyond any doubt, but the mechanism of their formation cannot be considered to have been fully clarified since two processes are possible:

(4) 
$$Hg^*(6^3P_1^0) + H_2 \longrightarrow H + H + Hg + 0.31 \text{ eV}$$

(6) 
$$Hg^* + H_2 \longrightarrow HgH + H + 0.80 \text{ eV}$$

The second process leading to the formation of mercury hydrate is energetically even more favourable. Moreover, mercury hydrate is really formed in the illuminated mixture—its lines are detected in the fluorescence spectrum. But this hydrate is not necessarily formed by process 6: its secondary formation is possible directly in the excited state:

$$Hg^* + H \longrightarrow HgH^*$$

and

$$HgH^* \longrightarrow HgH + hv$$

Possibly, both processes, 4 and 6, are responsible for the appearance of hydrogen atoms. The reaction of formation of hydrogen

atoms in question and some processes similar to it form the basis of numerous, so-called **photosensitized reactions**. The photosensitizer most widely employed is mercury.

In connection with this, let us examine in more detail the principal energy levels of the mercury atom that participate in this process. Figure 10.4 presents a simplified energy level diagram since the absorption spectrum of

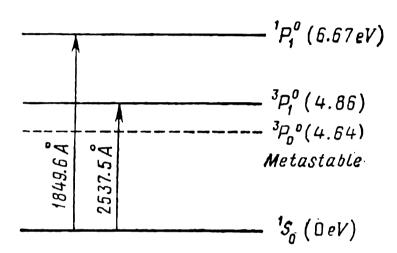


Fig. 10.4. Some energy levels of the mercury atom.

mercury vapour is simple: it consists mainly of two lines, 2537.5 and 1849.6 Å. From the ground state there are possible only two transitions associated with the absorption of light of these two wavelengths. An especially detailed study has been carried out on reactions caused by the absorption of the 2537.5 Å line, which is what we are concerned with in further treatment. When mercury vapour is illuminated by light of 2537.5 Å only atoms in the  $6^3P_1^0$  state are formed. In the absence of collisions (a low gas pressure, the absence of a foreign gas), they are subjected to only one conversion, namely, the fluorescence process which is the reverse of light absort tion. The 2537.5 Å line is observed during the fluorescence. As has been mentioned, the rate of this process obeys a first-order equation:

$$-\frac{d \left[\mathrm{Hg}^*\right]}{dt} = k_1 \left[\mathrm{Hg}^*\right] = I_f$$

where  $[Hg^*]$  is the concentration of excited atoms and  $I_f$  is the number of quanta of fluorescent radiation per unit volume per unit time. The various methods of determination of  $k_I$  have given, on

an average,

$$k_1 = 9.1 \times 10^6 \,\mathrm{sec}^{-1}$$

or the value of the inverse quantity  $\tau = 1/k_1 = 1.1 \times 10^{-7}$  sec (compare with the data of Table 10.3).

In the presence of a foreign gas, collisions take place and other processes become possible in addition to fluorescence. The most probable are the following:

- 1. A complete loss of the excitation energy through a collision of the second kind leading to the formation of the normal mercury atom.
- 2. A loss of 0.22 eV energy with a transition of the atom into the  $6^3P_0^0$  state. The mercury atom in this state is metastable, i.e., is not subject to an optical transition not associated with the violation of the selection rule. Nonetheless, in the absence of collisions it can radiate but with a small rate constant,  $k_1 \approx 10^3 \text{ sec}^{-1}$ ; accordingly, the average lifetime is  $10^{-3}$  sec. Besides, a collision can return it to the  $6^3P_1^0$  state with an increase of energy by 0.22 eV. The probability of this process, which can be evaluated by using the Boltzmann factor, will be at room temperature

$$e^{-E/RT} = 10^{-0.4343E/RT} = 10^{-0.4343 \times 0.22 \times 23,000/600} \approx 10^{-4}$$

This probability is not great and the principal way of disappearance of metastable atoms is perhaps their deactivation to their ground level by way of collisions of the second kind. There is ground for believing that this process is the main supplier of energy in photochemical, mercury-sensitized reactions. The supporting evidence is provided by a study of the process of quenching of the fluorescence of mercury vapour illuminated by light of 2537.5 Å by means of various gases. Without entering into the details, we note that the rate of quenching is estimated as follows. According to the collision theory, the rate constant of a bimolecular reaction is expressed, as known (7.11), by the following relation

$$k_{\rm H} = D_{\rm AB}^2 \left\{ 8\pi RT \left( \frac{1}{M_{\rm A}} + \frac{1}{M_{\rm B}} \right) \right\}^{1/2} e^{-\frac{E}{RT}}$$

where  $D_{AB}$  is the mean diameter of the colliding particles. When considering the quenching process, it is usually assumed that each collision is effective, i.e., E=0 and, using the experimentally found values of the constants, one solves Eq. (7.11) for  $D_{AB}^2$ , which is termed the **effective cross section** for quenching.

The effective cross sections for the quenching of fluorescence by nitrogen in the processes

$$\operatorname{Hg}\left(^{3}P_{1}^{0}\right) + \operatorname{N}_{2} \longrightarrow \operatorname{Hg}\left(^{2}P_{0}^{0}\right) + \operatorname{N}_{2}$$

and

$$\operatorname{Hg}\left({}^{3}P_{1}^{0}\right) + \operatorname{N}_{2} \longrightarrow \operatorname{Hg}\left({}^{1}S_{0}\right) + \operatorname{N}_{2}$$

are, respectively, equal to  $0.97 \times 10^{-16}$  and  $0.07 \times 10^{-16}$  cm<sup>2</sup>, i.e., during the formation of a metastable atom the cross section is supposed to be greater by a factor of 14. Nonetheless, certain gases, say hydrogen and oxygen, quench the fluorescence of mercury by the second process. Therefore, on the whole, it is difficult

now to answer the following question unequivocally: Which state of mercury,  ${}^{3}P_{1}^{0}$  or  ${}^{3}P_{0}^{0}$ , provides an energy as the source of the energy of photochemical reactions?

The afore-mentioned original observation by Cario and Franck was followed by a very large number of experimental investigations, which made use of excited mercury atoms in chemical reactions. Taylor and Marshall (1926-1927) studied the mercury-photosensitized interaction of hydrogen and oxygen. They found that the principal initial product is hydrogen peroxide. According to these authors, the primary process gives rise to hydrogen atoms and the peroxides that initiate the formation of a chain. Namely,

$$\operatorname{Hg}(^{3}P_{1}^{0}) + \operatorname{H}_{2} \longrightarrow \operatorname{H} + \operatorname{H} + \operatorname{Hg}(^{1}S_{0})$$
 $\operatorname{H} + \operatorname{O}_{2} \longrightarrow \operatorname{HO}_{2}$ 
 $\operatorname{HO}_{2} + \operatorname{H}_{2} \longrightarrow \operatorname{H}_{2}\operatorname{O}_{2} + \operatorname{H}$ 

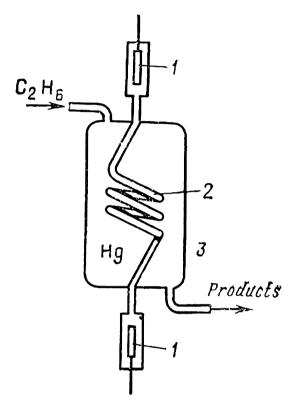


Fig. 10.5. Apparatus for conducting the photosensitized decomposition of ethane (schematic):

1—electrodes; 2—discharge tube with mercury vapour; 3—reaction vessel also containing mercury vapour and reacting substance.

There is no need to list all the reactions that have been studied; there are a very large number of such reactions. They include reactions involving mixtures of hydrogen with various inorganic substances: N<sub>2</sub>, CO, CO<sub>2</sub>, D<sub>2</sub>O, NH<sub>3</sub>, ND<sub>3</sub>, or with hydrocarbons, such as CH<sub>1</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>3</sub>H<sub>8</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>2</sub>. There have also been studied reactions involving oxygen-containing organic compounds, such as CH<sub>3</sub>OH, C<sub>2</sub>H<sub>5</sub>OH, CH<sub>3</sub>COCH<sub>3</sub>, etc. A large number of investigations on the photosensitized decomposition of various hydrocarbons have been conducted. For example, Steacie and Cunningham subjected ethane containing mercury vapour to the action of light from the mercury lamp (Fig. 10.5). In the reaction products there were detected considerable amounts of hydrogen, propane, butane and hexane — this in itself is an indication of

the complexity of the reactions involved. For instance, at a temperature of 88 °C and a pressure of 5 mm Hg, the reaction products contained:  $H_2$ , 45.6;  $CH_4$ , 15.4;  $C_3H_8$ , 10.7;  $C_4H_{10}$ , 8.6;  $C_6H_{14}$ , 19.7 molar per cent, and the quantum yield was equal to 0.28. With rise of temperature the quantum yield of decomposition almost doubled (0.53). The ratio  $H_2/CH_4$  decreased with rise of temperature and increased with increasing pressure.

Taylor and Marshall proposed the following mechanism for

the reaction:

(1) 
$$C_2H_6 + Hg^*(^3P_1^0) \longrightarrow C_2H_5 + H + Hg(^1S_0)$$
  
(2)  $H_2 + Hg^* \longrightarrow H + H + Hg$ 

(3) 
$$H + C_2H_6 \longrightarrow C_2H_5 + H_2 \qquad E \approx 8 \text{ kcal/mole}$$

$$(4) H + C_2H_5 \longrightarrow 2CH_3$$

(5) 
$$2CH_3 \longrightarrow C_2H_6$$

(6) 
$$CH_3 + C_2H_5 \longrightarrow C_3H_8$$

$$(7) 2C_2H_5 \longrightarrow C_4H_{10}$$

(8) 
$$2H + M \longrightarrow H_2 + M$$

(9) 
$$CH_3 + H + M \longrightarrow CH_4 + M$$

The increase of the quantum yield of the decomposition of ethane with rise of temperature is associated with the acceleration of reaction 3 which has an activation energy of about 8 kcal/mole. As a consequence, the role of the recombination process 8 is diminished. The rise of temperature also speeds up the process of "atomic cracking" 4, which reduces the ratio H<sub>2</sub>/CH<sub>4</sub>. When the initial pressure increases, the primary process 1 becomes faster and the consumption of hydrogen in reaction 2 is diminished. As a result, the yield of hydrogen increases. Besides, at higher pressures the process 3 becomes dominant as compared with process 4. This too increases the yield of hydrogen.

What has been just described is the result of a semiquantitative study of the photosensitized decomposition of hydrocarbons. Of course, on the basis of such a study of only a single reaction it is difficult to depict the actual mechanism of the conversion. Only through a comparison of the mechanisms supposed for different reactions can we exclude some elementary steps as improbable and, on the contrary, include the others. Thus, for example, the idea of atomic cracking of the type of process 4 in the Steacie-Cunningham mechanism is based, for one thing, on the results of investigations of the interaction of hydrogen atoms, which have been obtained by the Wood method in a discharge tube, with butane. The only product of this reaction at room temperature (apart from hydrogen) was methane. Its exclusive formation can

be explained, following Steacie and Brown, by a number of sequential reactions of atomic cracking:

$$(1) H + C_4H_{10} \longrightarrow C_4H_9 + H_2$$

$$(2a) H + C_4H_9 \longrightarrow C_3H_7 + CH_3$$

ОГ

(2b) 
$$H + C_4H_9 \longrightarrow C_2H_5 + C_2H_5$$

(3) 
$$H + C_3H_7 \longrightarrow C_2H_5 + CH_3$$

$$(4) \quad H + C_2H_5 \longrightarrow 2CH_3$$

(5) 
$$H + CH_3 + M \longrightarrow CH_4 + M$$

Reactions Induced by the Absorption of Light by Diatomic Molecules. Perhaps, there is no other photochemically active sub-

stance that has been so popular among chemists as chlorine. This is associated, first, with the fact that chlorine absorbs in the visible region and in the near ultraviolet region, and this makes it possible to use apparatus made of ordinary glass and molten quartz. Second, chlorine reacts with many substances with a considerable decrease of free energy, which in the long run makes possible the development of long chains. The quantum yields of many of the reactions involving chlorine

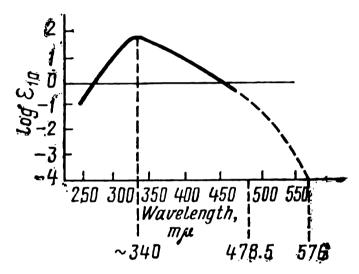


Fig. 10.6. The molar extinction coefficient  $(\epsilon_{10})$  of chlorine versus the wavelength.

reach very large values, amounting even to 106. Hence, to produce considerable quantities of products there is no need to use high radiation intensities.

The energy of dissociation of chlorine into two normal atoms is 2.475 eV. This energy corresponds to the radiation quanta having a wavelength of about 5000 Å or 500 m $\mu$ . So, a shorter-wavelength radiation provides an energy sufficient for the dissociation of Cl<sub>2</sub> into normal atoms. Figure 10.6 shows the dependence of the molar extinction coefficient ( $\epsilon_{10}$ ) of chlorine on wavelength. Beginning from long wavelengths, i.e., from about 576.0 m $\mu$ , there starts a weak absorption of discrete nature—the absorption spectrum has a banded structure. The latter converges at a wavelength of 478.5 m $\mu$ , which corresponds to the energy 2.59 eV and this is approximately 0.11 eV greater than the energy of dissociation into normal atoms. From this the conclusion is made that chlorine dissociates into a normal atom ( ${}^2P_{1/2}$ ) and an excited atom ( ${}^2P_{1/2}$ ) at the band convergence limit. The dissocia-

tion, however, occurs also at wavelengths longer than 478.5 mm. This can be explained by the absorption of light by molecules in a state of vibrational excitation or by the fact that the weak diffuse absorption in this region leads to the dissociation into normal atoms. Beyond the band convergence limit there begins a continuous absorption which reaches a maximum at about 340.0 mm. In this case the absorption coefficient is very large.\* In the region of continuous absorption the dissociation into a normal and an excited  $({}^2P_{1/2})$  atom probably takes place. It is however difficult to say whether the kinetics of photochemical reactions are affected by the fact that one of the atoms has a low, but noticeable excitation energy.

The most thoroughly studied photochemical reaction of chlorine is its interaction with hydrogen leading to the formation of hydrogen chloride. This reaction has been shown in many works to exhibit characteristic features. The following are some of these features:

1. The *induction period* is often observed, i.e., for a certain time after the illumination is started the reaction proceeds very slowly or does not occur at all. This phenomenon is ascribed to the presence of contaminants; only after these are removed does the normal development of the reaction begin.

2. The reaction velocity is inversely proportional to the concentration of oxygen when it is present in small amounts (from 0.09

to 1.00 mol. per cent).

3. There is evidently no explicitly pronounced photochemical threshold, though at wavelengths longer than 500 mµ the reaction

proceeds very slowly.

4. The quantum yield of the reaction is high. According to the data obtained by Bodenstein, it is close to  $10^6$ . The quantum yield, however, varies strongly, depending on the content of impurities and it is difficult to prepare two mixtures which would give identical  $\gamma$  values.

5. The data on the effect of light intensity are contradicting. Possibly, the reaction rate grows more slowly than the light in-

tensity.

6. On the whole, in the presence of oxygen the empirical equation for the reaction velocity, according to the data of Bodenstein and Unger (1930), has the form

$$\frac{d [HCI]}{dt} = \frac{kI_a [H_2] [CI_2]}{m [CI_2] + [O_2] \left\{ [H_2] + \frac{[CI_2]}{10} \right\}}$$
(10.25)

<sup>\*</sup>  $\epsilon_{10} \approx 100$ . This means that at 1 atm (i.e., at a concentration of 1/22.4 moles/litre) the intensity decreases by half with a layer only 0.067 cm thick  $\left(I/I_0 = 10^{-\epsilon_{10}cl}, \log 1/2 = -\epsilon_{10}cl; 100l/22.4 = 0.301 \text{ or } l = 0.067\right)$ .

In a better keeping with this equation is the following scheme \* (Chering, 1921):

(1) 
$$Cl_2 + hv \longrightarrow Cl + Cl$$
  $l_a\gamma_1$   
(2)  $Cl + H_2 \longrightarrow HCl + H$   $k_2$   
(3)  $H + Cl_2 \longrightarrow HCl + Cl$   $k_3$   
(4)  $H + O_2 \longrightarrow HO_2$   $k_4$   
(5)  $Cl + O_2 \longrightarrow ClO_2$   $k_5$ 

The nature of X remains to be obscure; it may be silicon com-

pounds, perhaps, even involatile.

(6)  $Cl + X \longrightarrow ClX$ 

Applying the steady-state method to hydrogen and chlorine atoms, we have

 $k_{\rm S}$ 

$$k_2 [Cl] [H_2] = k_3 [H] [Cl_2] + k_4 [H] [O_2]$$
  
 $2I_a\gamma_1 + k_3 [H] [Cl_2] = k_2 [Cl] [H_2] + k_5 [Cl] [O_2] + k_6 [Cl] [X]$ 

or

$$[C1] = \frac{k_3 [H] [C1_2] + k_4 [H] [O_2]}{k_2 [H_2]} = \frac{2I_a \gamma_1 + k_3 [H] [C1_2]}{k_2 [H_2] + k_5 [O_2] + k_6 [X]}$$

Having thus eliminated [Cl] and neglecting the product  $k_4k_5$ [H] [O<sub>2</sub>]<sup>2</sup> because of the small concentration of oxygen, we find the concentration of hydrogen atoms:

[H] = 
$$\frac{2k_2\gamma_1I_a[H_2]}{k_3k_6[CI_2][X] + [O_2]\{k_2k_4[H_2] + k_3k_5[CI_2] + k_4k_6[X]\}}$$

Then, since the chains are long, the rate of formation of hydrogen chloride may be expressed by the doubled rate of reaction 3:

$$\frac{d [HCI]}{dt} = 2k_3 [H] [Cl_2] =$$

$$= \frac{4k_2k_3\gamma_1I_a [H_2] [Cl_2]}{k_3k_6 [Cl_2] [X] + O_2 \{k_2k_1 [H_2] + k_3k_5 [Cl_2] + k_1k_6 [X]\}} =$$

$$= \frac{4\frac{k_3}{k_1} \gamma_1I_a [H_2] [Cl_2]}{\frac{k_3k_6}{k_2k_4} [Cl_2] [X] + O_2 \{[H_2] + \frac{k_3k_5}{k_2k_4} [Cl_2] + \frac{k_6}{k_2} [X]\}}$$

The last expression coincides with the Bodenstein-Unger empirical equation, except for the term  $(k_6/k_2)[X]$  in braces, which is hardly significant.

The Formation of Hydrogen Bromide. The energy of dissociation of bromine into two normal atoms  $(^3P_{1/2})$  is 1.971 eV, so that for this process to occur, a quantum energy of radiation of wavelength shorter than 6288 Å is sufficient. The intensity maximum

<sup>\*</sup> The mechanism of the oxygen-free reaction (the Nernst mechanism) was given in Chapter 9.

of continuous absorption lies at about 4100 Å; the dissociation involved probably gives rise to a normal and an excited  $(^3P_{1/2})$  atom \*.

When a mixture of bromine and hydrogen is exposed to light, there develops a chain process leading to the formation of hydrogen bromide, the kinetics of which \*\* are consistent with the following mechanism:

(1) $Br_2 + hv \longrightarrow Br + Br$	$\gamma_1 I_{\epsilon}$
$(2) Br + H_2 \longrightarrow HBr + H$	$k_2$
$(3) H + Br_2 \longrightarrow HBr + Br$	$k_3$
$(4) H + HBr \longrightarrow H_2 + Br$	$k_4$
(5) $Br + Br + M \longrightarrow Br_2 + M$	$k_5$

The application of the steady-state method results in the following expression for the rate of the reaction being measured:

$$\frac{d \text{ [HBr]}}{dt} = \frac{2k_2 \text{ [H}_2] (\gamma_1 I_a)^{1/2}}{k_5^{1/2} M^{1/2} \left\{ 1 + k_4 \frac{\text{[HBr]}}{\text{[Br}_2]} \right\}}$$
(10.26)

which differs from the equation given earlier for a thermal reaction, (3.72), by the presence of the factor  $(\gamma_1 I_a)^{1/2}$  in place of  $[Br_2]^{1/2}$ . This factor corresponds to the third limiting case, namely, the termination of chains by a homogeneous recombination of the type

$$D_1 + D_1 + M \longrightarrow A + M$$

Reactions of the Simplest Hydrocarbons. Methane absorbs light only in the short-wavelength ultraviolet region. The absorption spectrum of methane is entirely continuous; the intensity maximum lies between 1200 and 1300 Å. With a continuous absorption of the type observed in methane it is necessary to assume that the excited states are repulsive states (Fig. 10.2c). Therefore, the light absorption act is accompanied by an immediate dissociation. The most probable is the primary formation of the methyl radical:

$$CH_4 + hv \longrightarrow CH_3 + H$$

A photochemical study has been carried out through the use of the xenon 1295 and 1470 Å lines. The quantum yield with respect to hydrogen at room temperature and a pressure of about 1 atm ranges from 0.35 to 0.50. Among the products there were found acetylene, ethylene, ethane, and hydrocarbons containing from three to five carbon atoms. With the lapse of time the quantum

\*\* The kinetics of this reaction were studied by M. Bodenstein and H. Lüt-kemeyer (1924).

<sup>\*</sup> Just as in the case of chlorine, there is no ground for ascribing substantially differing reactivities to these atoms.

TABLE 10.4. Data on Some Photochemical Reactions

Peactants	Products	Quantum yield	Exposure condi- tions, etc.	Temperature coefficient
U <sub>2</sub>	$O_3$	$\gamma_{\rm O_3} = 1.14 - 2.0$	2530, 2070, 1770, 1470; 1-300 atm	<1
СО	$CO_2, C_3O_2$	$\gamma_{\rm CO} = 1$	1295, 1 atm	_
$CO + H_2$	HСНО, (НСО)₂	$\gamma_{-CHO} = 0.5$	1470, 1295	
NO	$N_2$ , $O_2$	$\gamma_{\rm NO} = 0.75$	<1900, ca. 1830	
HCI	H <sub>2</sub> , Cl <sub>2</sub>	Very low	ca. 2000	>1
I IBr	H <sub>2</sub> , Br <sub>2</sub>	$\gamma_{IIBr} = 2$	<2800	>1
HII	H <sub>2</sub> , I <sub>2</sub>	$\gamma_{\rm HI}=2$	<3500	
$\mathbb{O}_2$ , $\mathbb{H}_2$	НСІ	Very high	5400-3000	1.1-1.2
Cl₂, CH₄	HCI, CH <sub>3</sub> CI, CH <sub>2</sub> CI <sub>2</sub> , CHCI <sub>3</sub> , CCI <sub>4</sub>	High	5400-3000	1.1
Cl <sub>2</sub> , C <sub>2</sub> H <sub>4</sub>	C <sub>2</sub> H <sub>2</sub> Cl <sub>2</sub> , HCl, and substitution products	High	4358	
Br <sub>2</sub> , H <sub>2</sub>	HBr	l at 200 °C and very low at 25 °C	6000	2.6
$Br_2$ , $C_2H_2$	$C_2H_2Br_2$	High	4358-5791	1
CH;	$H_2$ , $C_2H_2$ , $C_2H_4$ , $C_2H_6$	$\gamma_{\text{H}_2} = 0.35 \text{-} 0.50$	1470, 1295, 1 atm	
$C_2H_6$	$H_2$ , $C_2H_2$ , $C_2H_4$ , $CH_4$ , $C_3H_8$ , $C_4H_{10}$	$\gamma_{II_2} = 0.96$	1470, 1295, 180 mm Hg	_
C₂H₂	Yellow polymer cuprone	γ ≈ 8±2	2150, $p = 100$ mm Hg	1.25
C <sub>2</sub> H <sub>4</sub>	H <sub>2</sub> , CH <sub>1</sub> , C <sub>2</sub> H <sub>2</sub> , polymers		Hg—arc, Al, Zn—spark	-
$C_6H_6$	$H_2$ , $(C_6H_5)_2$	-	2200, Al—spark	
НСНО		$\gamma_{CO}$ =0.9 at 110° $\gamma_{CO}$ =2.9 at 200° $\gamma_{CO}$ =100 at 350°	3100-3500	_

yield increases, which points to the increasing absorption of light

by the products.

The illumination of ethane with the same xenon lines leads to the formation of a large number of products. The quantum yields with respect to the various products obtained are as follows:

$$\gamma_{\rm H_2} = 0.96; \quad \gamma_{\rm C_2H_4} = 0.56; \quad \gamma_{\rm C_2H_2} = 0.20; \quad \gamma_{\rm CH_4} = 0.05; \quad \gamma_{\rm C_3H_8+C_4H_{10}} = 0.01$$

Since in the presence of carbon monoxide there is formed acetone, the most probable primary process is the splitting of ethane into two methyl radicals:

$$C_2H_6 + hv \longrightarrow 2CH_3$$

Table 10.4 summarizes data on some photochemical reactions, a part of which have been studied only qualitatively. It should be noted that, on the whole, the rates of photochemical reactions, as a rule, depend little on temperature. An exception is the formation of hydrogen bromide, the quantum yield of which is low at room temperature and approaches unity with rise of temperature.

# Kinetics and Mechanism of Reactions in Electrical Discharges\*

#### 11.1. General Treatment

The kinetics of reactions taking place in electrical discharges have been most thoroughly studied for the following processes:

$$2CH_{4} \longrightarrow C_{2}H_{2} + 3H_{2}$$

$$N_{2} + O_{2} \longrightarrow 2NO$$

$$3O_{2} \longrightarrow 2O_{3}$$

$$H_{2} + O_{2} \longrightarrow H_{2}O_{2}$$

It is these reactions that we shall be mainly concerned with in this chapter.

The first stage in the development of the kinetics of gas reactions in electrical discharges (the twenties of this century) is characterized by attempts to draw an analogy between electrical gaseous reactions and electrolysis in solution. The proportionality observed in some cases between the amount of reacting substance and the current strength led to the formulation of the law of electrochemical equivalence analogous to the Faraday laws.

It was however soon found that the Faraday laws are in general inapplicable to reactions occurring in electrical discharges. This can be illustrated by a simple example. In electrolysis, the amount of substance deposited on the electrodes per unit time depends only on the current strength and is completely independent of the distance between the electrodes, the variation of which leads only to the change of the voltage required for the given current strength to be maintained in the electrolytic cell. A quite different situation obtains during reactions in an electrical discharge. For instance, in a glow discharge the amount of reacting substance, other conditions being equal, is approximately proportional to the distance between the electrodes. The voltage on the

<sup>\*</sup> This chapter has been written on the basis of the investigations carried out in the Laboratory of Catalysis and Gas Electrochemistry in the Moscow State University by N. I. Kobozev, E. N. Yeremin, Yu. V. Filippov, Yu. M. Emelyanov, A. N. Maltsev and also by S. S. Vasiliev *et al.* 

electrodes varies in proportion to this distance too \*. On the basis of this observation and of the proportionality between the amount of reacting substance and the current strength there has been formulated the basic proposition which supplements the well-known laws of chemical kinetics for reactions in electrical discharges: The rate of a chemical reaction in a given type of electrical discharge is proportional to the discharge power \*\*.

The restriction implied by the expression "in a given type of electrical discharge" should be understood in the sense that the change of the power must not lead to the change of the type of discharge. The proportionality factors for different types of discharge for the same reaction may have quite different values. For example, the glow discharge at low pressures is very little effective for the conversion of methane into acetylene, and the arc is quite effective at moderate pressures. Therefore, if the power change caused, for example, by the change of pressure and current, turns the glow to the arc discharge, the proportionality factor sharply increases.

In studying the kinetics of reactions in an electrical discharge, a difficulty was encountered, which was associated with the practical impossibility of precise determination of the reaction time. The point is that the actual volume of the reaction zone is unknown in most cases, except possibly for the barrier discharge in an ozonizer.

In the mid-thirties Kobozev, Vasiliev, and Yeremin worked out the main principles of the kinetics of reactions in electrical discharges; they also suggested that the volume of the reaction zone be included in the rate constant, i.e., that the reaction time in kinetic equations be replaced by a proportional quantity—the inverse rate of flow, 1/v, through the reaction vessel. These authors introduced the concept of the specific energy U/v as the quantity determining the course of a reaction in the discharge.

In the subsequent sections we shall consider the application of the basic principles, which have just been outlined, to the study of the kinetics of individual reactions.

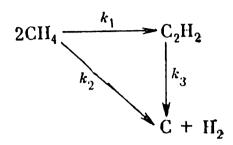
### 11.2. Kinetics of Electrocracking of Methane

As experiment shows, apart from the principal reaction of formation of acetylene, the electrocracking of methane also involves a number of other reactions: the formation of ethylene, ethane,

\*\* This regularity is close in physical meaning to the van't Hoff law for photochemical reactions (Chapter 10),

<sup>\*</sup> This statement is valid for a discharge of a sufficient length, when the cathodic potential drop, which remains constant, is small as compared with the total voltage on the electrodes.

and diacetylene, the decomposition of hydrocarbons into their elements, etc. The kinetics of the conversion of methane and of the accumulation of acetylene, however, may, at a first approximation, be represented by the following scheme, independently of the mechanisms of the reactions involved:



where  $k_1$ ,  $k_2$ , and  $k_3$  are the first-order rate constants for the corresponding reactions, which are independent of the power U.

This scheme takes into account the formation and decomposition of acetylene and also the decomposition of methane into the elements. Methane thus participates in two parallel reactions, and acetylene is an intermediate in two consecutive reactions. The concentration of acetylene, or the extent of conversion of methane into acetylene, must, according to the above scheme, pass through a maximum with increasing U/v, which is completely supported by experiment. To derive the kinetic equations, let us represent, in a simplified manner, the reaction zone in the form of a cylinder into which  $N_0$  moles of methane is fed. Let us pick out in this cylinder an infinitely thin layer in which the amount of methane decreases from  $N_{\rm CH_1}$  to  $N_{\rm CH_2} - dN_{\rm CH_3}$  during the residence time dt. Then, the overall rate of conversion of methane in this layer will be written in the form

$$-\frac{dN_{\text{CH}_4}}{dt} = (k_1 + k_2) UN_{\text{CH}_4}$$
 (11.1)

and the rate of accumulation of acetylene will be given by

$$\frac{dN_{\text{C}_2\text{H}_2}}{dt} = \frac{1}{2} k_1 U N_{\text{CH}_4} - k_3 U N_{\text{C}_2\text{H}_2}$$
 (11.2)

Equations (11.1) and (11.2) take account of the proportional relation between the reaction rate and the discharge power.

Integrating expression (11.1) from 0 to t and from  $N_0$  to  $N_{CH_4}$ , we obtain

$$N_{\text{CII}_4} = N_{\dot{0}} e^{-(k_1 + k_2) Ut} \tag{11.3}$$

According to what has been said earlier, we replace the reaction time t by the inverse rate of gas flow 1/v (upon replacement the dimensions of the constants  $k_1$  and  $k_2$  are, of course, changed) and after simple rearrangements we get an expression for the

overall rate of conversion of methane,  $\Delta$ :

$$\frac{N_0 - N_{\text{CH}_4}}{N_0} \equiv \Delta = 1 - e^{-(k_1 + k_2) \frac{U}{v}}$$
 (11.4)

Substituting  $N_{\rm CH_4}$  from Eq. (11.3) into Eq. (11.2) and integrating, we obtain an expression for the extent of conversion of methane into acetylene:

$$\frac{2N_{C_2H_2}}{N_0} = \gamma = \frac{k_1}{k_1 + k_2 - k_3} \left[ 1 - e^{-(k_1 + k_2 - k_3)\frac{U}{v}} \right] e^{-k_3\frac{U}{v}}$$
(11.5)

We now express, as a function of the specific energy, the consumption of energy per cubic metre of acetylene reduced to standard conditions; then,

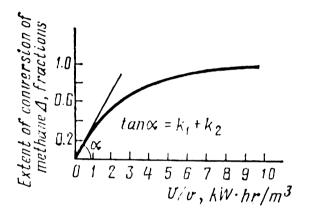


Fig. 11.1. The degree of conversion (extent of reaction) of methane in the discharge versus the specific energy.

$$\frac{U}{v} \cdot \frac{2}{v} \equiv \alpha =$$

$$= \frac{2(k_1 + k_2 - k_3) \frac{U}{v} e^{\frac{k_1}{v} \frac{U}{v}}}{k_1 \left[1 - e^{-(k_1 + k_2 - k_3) \frac{U}{v}}\right]} kW \times \frac{1}{\sqrt{\frac{1}{v}}} \left[1 - e^{-(k_1 + k_2 - k_3) \frac{U}{v}}\right]$$

(here the power U is expressed in kW, and the rate of gas flow v in  $m^3/hr$ ).

Let us now consider the dimensions and the physical meaning

of the constants  $k_i$  in the final formulas (11.4), (11.5), and (11.6). Since the constants are included as cofactors together with the specific energy in the dimensionless exponents, their dimensions are the inverse of the dimensions of U/v, i.e., are essentially different from the dimensions of the rate constants in conventional chemical kinetics. Thus, if U/v is expressed in  $kW \cdot hr/m^3$  of gas reduced to standard conditions, the dimensions of  $k_i$  will be  $m^3/kW \cdot hr$ .

The elucidation of the physical meaning of the constants may be approached in the following manner. Expanding the function (11.4) into a power series of U/v, we have

$$\Delta = (k_1 + k_2) \frac{U}{v} - \frac{(k_1 + k_2)^2 \left(\frac{U}{v}\right)^2}{1 \times 2} + \frac{(k_1 + k_2)^3 \left(\frac{U}{v}\right)^3}{1 \times 2 \times 3} - \dots$$
 (11.7)

If the ratio U/v is small, say, if the experiment is carried out at high rates of gas flow, then we may neglect all the terms in

this series, except the first; then

$$\Delta = (k_1 + k_2) \frac{U}{v} \tag{11.8}$$

or

$$k_1 + k_2 = \frac{\Delta \cdot v}{U} \tag{11.9}$$

Here  $\Delta v$ , the product of the flow rate of methane (m³/hr) by the overall extent of its conversion  $\Delta$ , is as a whole the total amount (in cubic metres) of methane reacted in the discharge per hour. The quantity U is the discharge power. Hence, the fraction on the right-hand side of Eq. (11.9) is the amount of methane, converted in the discharge for 1 hour, per 1 kW of the discharge power, or the number of cubic metres of methane reacted per 1 kW·hr of energy of the discharge. It should be remembered, however, that relation (11.8) is valid only at small

values of U/v. Therefore, the constants  $k_1$  and  $k_2$  represent the amount of methane converted in the corresponding directions at low specific energies per unit quantity of electrical energy consumed in the

discharge.

What has been said above can be explained by reference to Fig. 11.1. Here the curve shows the dependence of the overall extent of conversion of methane on the specific energy in accordance with relation (11.4), and the straight line is a tangent to the curve at the coordinate origin and is described by relation

Inergy consumed & Alt: hr/m³ C2 H2

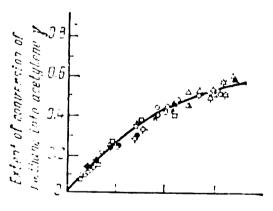
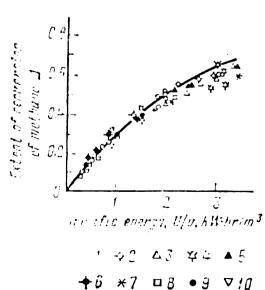


Fig. 11.2. The overall degree of conversion (extent of reaction) of methane, Λ, the degree of conversion into acetylene, γ, and the consumption of energy per 1 m³ of acetylene, α, versus the specific energy U/v at different currents, pressures and distances between the electrodes:

	1	2	3	4	5
P, mm Hg i, A l, cm	42-46	42 46	42-46	42-16	42-46
	0.5	1.0	3.5	5.0	5.0
	54.1	54.1	50.5	55.1-55.5	42 <b>.</b> 0
	б	7	8	9	10
P, mm Hg	42-46	42-46	75	100	150
i, A	1.0	5.0	0.5	0.5	0.5
l, cm	18.0	29.5	32.5	32.5	18.0



(11.8). From Fig. 11.1 it is seen that at small U/v corresponding to small degrees of conversion,  $\Delta$  is proportional to the specific energy. The proportionality factor, i.e., the slope of the straight line, is equal to the sum  $k_1 + k_2$ .

From the foregoing it is clear that the constants under discussion characterize the capacity of the discharge to effect a

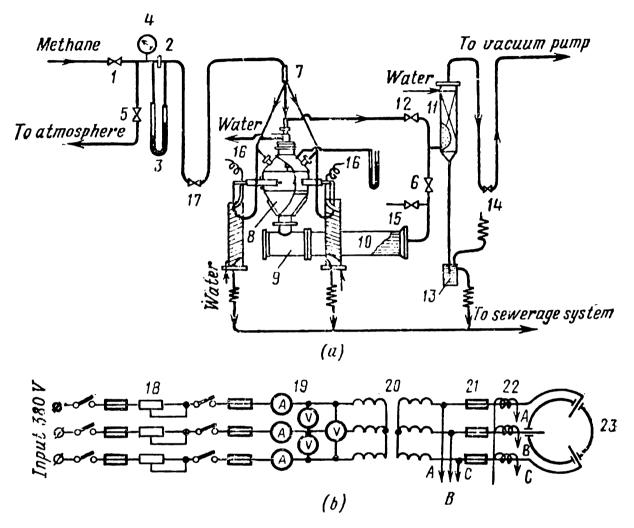


Fig. 11.3. Schematic of apparatus for the electrocracking of methane at lowered pressure:

(a)—schematic of the technological section of the apparatus: 1, 5, 6, 12, 14, 17—valves; 2—diaphragm; 3—differential manometer; 4—manometer; 7—gas header; 8—reactor; 9—T-joint; 10—cooler; 11—gas scrubber; 13—hydraulic seal; 15—sampling for analysis; 16—high voltage of three-phase current; (b)—circuit diagram of electric instruments: 18—rheostats; 19—measuring bank of the primary circuit; 20—power transformer; 21—to the measuring transformer HOM-6; 22—current transformer; 23—reactor.

chemical conversion per unit energy consumed. In connection with this, it has been suggested that these constants be termed the energy efficiency of the chemical action of the discharge.

Figure 11.2 compares the results of calculations made by means of formulas (11.4), (11.5) and (11.6) with experimental data on the electrocracking of methane to give acetylene. In this case, experiments have been conducted in a three-phase arc at lowered pressure which ranged, in different series of experiments, from 40 to 150 mm Hg. The diagram of the enlarged apparatus used in this case is shown in Fig. 11.3.

The current of the arc ranged from 0.5 to 5 A and the distance between the electrodes from 55 to 18 cm. In spite of this variety of experimental conditions, the experimental data, which are presented in the form of the dependences of the total degree of conversion of methane  $\Delta$ , the extent of conversion to acetylene  $\gamma$  and the energy consumption per 1 m³ of acetylene,  $\alpha$ , on the specific energy U/v (Fig. 11.2) are satisfactorily described by formulas (11.4), (11.5), and (11.6).

The constants determined from the experimental data in this case are equal to:  $k_1 = 0.317$ ;  $k_2 = 0.026$ ;  $k_3 = 0.058$  m<sup>3</sup>/kW·hr.

The total energy efficiency of the discharge for the conversion of methane, i.e., the sum  $(k_1 + k_2)$  is equal in this case to  $0.343 \text{ m}^3/\text{kW} \cdot \text{hr}$ .

The variation of the pressure of the gas in which the discharge burns, may lead to the transformation of one form of the discharge to another (the glow to the arc discharge, etc.). These changes of the discharge shape, in their turn, lead to the change of its energy efficiency with respect to a particular chemical reaction. This is one aspect of the problem, which undoubtedly deserves a special study. On the other hand, one can speak of the effect of the pressure on the course of the reaction provided that a given shape of the discharge (say, the arc) is not changed. If, by varying the pressure of methane, the change of the discharge configuration is ignored, both the positive and the negative effect of the pressure on the course of the electrocracking reaction may be observed. For example, as has already been mentioned, the increase of the pressure from very small values at low current values results in a quite considerable increase in the energy efficiency. But when the pressure increases further, especially at high current values, i.e., under the conditions of utmost practical importance, a different situation probably obtains.

A study of the electrocracking process conducted in a quite different type of apparatus, which makes it possible to carry out the process at pressures up to 760 mm Hg and higher, has shown a significant decrease of the energy efficiency of the discharge. Thus, at pressures 70-100 mm Hg it has been found that  $k_1 + k_2 = 0.373$  m³/kW·hr, i.e., a value that practically coincides with the previous one. At a pressure close to 760 mm Hg the efficiency decreased almost twice:  $k_1 + k_2 = 0.196$ . It is interesting to compare this phenomenon with the considerable acceleration of the thermal conversion of methane into acetylene with decreasing pressure. Thus, the energy efficiency of the discharge may be regarded as a constant that characterizes the electrocracking process under given conditions (pressure, a high-voltage arc).

The effect of an impurity of hydrogen in methane on the electrocracking process has been studied at various pressures and

with various discharge configurations. It has also been investigated at atmospheric pressure in a single-phase a-c arc in a laboratory reactor. The starting materials used were concentrated methane (93-96 vol. per cent of  $CH_4$ ) and mixtures of methane and hydrogen in the following proportions:  $CH_4/H_2 = 69.4/27.2$ ; 59.1/37.2, and 48.4/48.4. The results obtained (Fig. 11.4) show that the overall extent of conversion of methane  $\Delta$  is, independent-

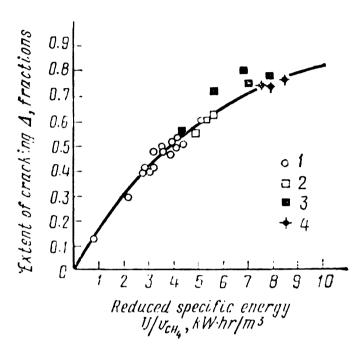


Fig. 11.4. The degree of conversion of methane versus the reduced specific energy for different amounts of hydrogen in the original mixture

	vol. % CH	vol. % H
1	93-96	0
2	69.4	27.2
3	59.1	37.2
4	48.8	48.4

ly of the hydrogen concentration, a function of the so-called reduced specific energy U/v. This energy is defined in this case as the ratio of the discharge power to the rate of flow of methane or, what is the same thing, to the total flow rate of the mixture, v, multiplied by the volume fraction of methane in the mixture.

The curve in Fig. 11.4 has been calculated by formula (11.4) with the appropriate replacement of the total specific energy by the reduced energy. It has been found that the sum of the kinetic constants,  $k_1 + k_2$ , is equal to 0.184 m<sup>2</sup>/kW·hr. Thus, it turns out that the energy efficiency of the discharge, i.e., in accordance with relation (11.9) the amount of methane converted per unit

quantity of consumed energy at  $U/v \rightarrow 0$ , does not depend on the extent of dilution of methane by hydrogen. In other words, hydrogen is, so to say, a quite inert diluent which does not itself require energy. In fact, considerable quantities of discharge energy are consumed, say, for the dissociation of hydrogen molecules into atoms, but probably this energy is further used in some way for the cracking reaction.

We have just described cases where the specific energy determines the course of reaction unambiguously. This, however, refers to the well-defined discharge of a definite type and is not always observed. It happens that the change of the specific energy, say, as a result of an increase of the discharge power or of a change in the condition of the electrodes, etc., leads to a different discharge configuration, which has a substantially different efficiency with respect to the reaction under study. In other words, in such

cases the specific energy criterion is insufficient for describing the kinetics. An example is the curve of the total extent of conversion of methane versus U/v, which has been obtained in experiments with mixtures of methane and ethylene (1:1) at a pressure of

18 mm Hg and a current of about 160 mA (Fig. 11.5). As seen, the function  $\Delta = f(U/v)$ for ethylene is described by a general kinetic single | firstorder curve (11.4) with  $k_1$  +  $+ k_2 = 0.500$  litre/W·hr. the same time, on the  $\Delta$  curve for methane there is a kink due evidently to a change in the discharge efficiency. Perhaps, the increase of the efficiency is the result of the change in the condition of the walls of the discharge tube and of the electrode surfaces (the deposition of carbon). The experimental described by two data are first-order curves (shown by

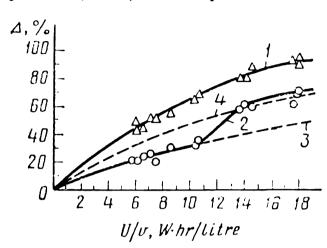


Fig. 11.5. The degree of conversion of methane and ethylene in the mixture versus the specific energy (P = 18 mm Hg):

1—degree of conversion of ethylene:  $2-de^2$  gree of conversion of methane; 3 and 4—overall conversion of methane calculated from the average values of  $(k_1+k_2)$  for two series of experiments.

dotted lines) corresponding to the constants which have the following values:  $k_1 + k_2 = 0.0387$  and  $k_1 + k_2 = 0.065$  litre/W·hr.

# 11.3. Kinetics and Mechanism of Reactions Involving the Conversion of Hydrocarbons at Low Pressures in the Glow Discharge

The data given earlier on the kinetics of conversion of methane refer mainly to the shapes of the discharge (an arc and a glow discharge at a high current) when the major product is acetylene. These conditions are of interest from the practical point of view but are not suitable for the study of the intermediate steps and the mechanism of the reaction.

A study of the kinetics of the conversion of the simplest hydro-carbons—acetylene, ethylene, and ethane (0.7-1.7 mm Hg) and methane (up to 3 mm Hg)—in a glow discharge at low pressures has been carried out on the apparatus shown in Fig. 11.6. The reaction products were condensed as soon as they left the discharge tube in traps at the temperature of liquid nitrogen and were subjected to chromatographic analysis.

The Kinetics of Conversion of Acetylene. Figure 11.7 is a plot of the overall extent of conversion of acetylene,  $\Delta_{C_2H_2}$  versus the

specific energy. The solid curve is calculated by the equation

$$\Delta_{C_2\Pi_2} = 1 - e^{-k_4 (U/v)} \tag{11.10}$$

that is, by the first-order law with an average value of  $k_4 = 0.0855$  litre/W·hr. As can be seen, the calculated curve coincides satisfactorily with the experimental data. The reaction proceeds rapidly and is accessible for study only at the lowest current

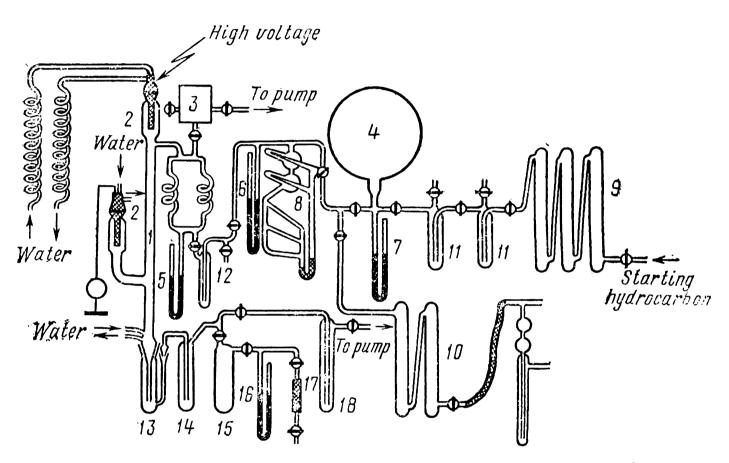


Fig. 11.6. Schematic of apparatus for reactions of conversion of gaseous hydrocarbons in the low-pressure glow discharge:

I—discharge tube: 2—electrodes; 3—McLeod pressure gauge; 4—container for storage of pure hydrocarbon; 5, 6, 7—manometers; 8—rheometer; 9, 10, 11—system for purification of hydrocarbons; 12, 13, 14, 15, 18—traps cooled by liquid nitrogen; 17—sampling of the condensate delivered from traps for chromatographic analysis.

used (32 mA). The main products of the conversion of acetylene are solid polymers having a brown colour. Among the gaseous products were ethane, ethylene (the extent of conversion  $\gamma$  does not exceed 0.1 per cent), small amounts of propane and propylene, and also the gaseous derivatives of acetylene (more than 10 in number).

The kinetics of the conversion of acetylene in mixtures with hydrogen  $(C_2H_2/H_2 = 1:1, 1:1.8, \text{ and } 1:5)$  has also been studied. The experimental data are also satisfactorily described by first-order equations of the same form as expression (11.10) on condition that  $v = v_{C_2H_2}$ , i. e., is the partial flow rate of acetylene (litre/hr under normal conditions). In the case of the greatest dilution (1:5) the second-order constants exhibit better constancy.

If we compare the reaction rates for the first-order constants, then, on the basis of the values  $k_4 = 0.0085$  (undilute acetylene),  $k_4 = 0.065$  (1:1),  $k_4 = 0.050$  (1:1.8), and  $k_4 = 0.031$  litre of  $C_2H_2/W\cdot hr$  (1:5), we may speak of the retardation of the decomposition of acetylene by hydrogen. This accounts for the presence of acetylene under the conditions of the electrocracking of methane when the acetylene formed is dilute—per one volume of acetylene there is produced a minimum of 3 volumes of hydrogen. In

experiments, when the dilution with hydrogen reached 1.5, the amount of hydrogenation products, especially of ethane increased appreciably ( $\gamma_{C_2H_6} \approx 5$  per cent);  $\gamma_{C_2H_4} \approx 3$  per cent. The amounts of propane, propylene, and gaseous derivatives also increased.

The Mechanism of Conversion of Acetylene. In discussing the mechanism of the conversion of acetylene, one takes into account that in a glow discharge at low pressures, which is characterized by the presence of high electronic and low molecular temperatures, there are created favourable conditions for the formation of considerable amounts of free radicals and atoms. In the case of acetylene, two pathways are pos-

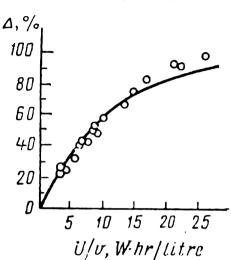


Fig. 11.7. The degree of conversion of acetylene versus the specific energy. The curve has been calculated from the average value of k = 0.086 litre/W · hr.

sible for the decomposition of molecules excited by electron impacts:

(1) 
$$C_2H_2 \longrightarrow C_2H + H \quad \Delta H^0 = 113-115 \text{ kcal/mole}$$

(2) 
$$C_2H_2 \longrightarrow 2CH$$
  $\Delta H^0 = 230 \pm 2 \text{ kcal/mole}$ 

Both reactions are strongly endothermic, but reaction 1 is more probable and may well become the primary step of the process.\* Atomic hydrogen in its turn can enter into interaction with the starting acetylene:

$$(3) \quad C_2H_2 + H \longrightarrow C_2H_3$$

(4) 
$$C_2H_2 + H \longrightarrow C_2H + H_2$$

Under the conditions studied, reaction 4 plays, evidently, a more important part than reaction 3, which leads to the hydrogenation of acetylene since the hydrogenation products—ethylene and ethane—were detected in negligible quantities. The radicals  $C_2H$  resulting from reactions 1 and 4 enter further into reaction with

<sup>\*</sup> It should be noted that under similar conditions there occurs, for example, the dissociation of hydrogen into the atoms with  $\Delta H^0$  being equal to 103 kcal/mole.

acetylene, this reaction leading eventually to the polymerization of acetylene:

(5) 
$$C_2H + C_2II_2 \longrightarrow C_4H_3$$

(6) 
$$C_4H_3 + C_2H_2 \longrightarrow C_6H_5$$
, etc.

They can, to a certain extent, participate also in the formation of diacetylene found among the reaction products:

$$2C_2H \rightarrow C_4H_2$$

Further decomposition is also possible

$$2C_2H \longrightarrow 2C_2 + H_2$$

under the influence of electron impacts: particles of C2 were de-

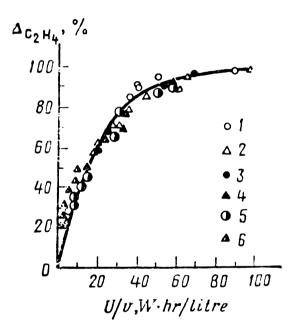


Fig. 11.8. The degree of conversion of ethylene against the specific energy at various currents (mA):

The curve has been calculated from the average value of the first-order

tected spectroscopically in the reaction of acetylene in the discharge.

By choosing the most probable processes for kinetic calculations we obtain the following list of reactions for the mechanism of the conversion of acetylene undiluted with hydrogen:

$$(1) \quad C_2H_2 \xrightarrow{k_1} C_2H + H$$

$$(4) \quad C_2H_2 + H \xrightarrow{k_4} C_2H + H_2$$

(5) 
$$C_2H + C_2H_2 \xrightarrow{k_7} C_2H_3$$

$$(7) \quad H \xrightarrow{k_7} \frac{1}{2} H_2$$

Here it is supposed that the recombination of atomic hydrogen occurs predominantly on the wall since under the conditions of low pressures the triple collision required for the recombination of the hydrogen atom in the bulk is hardly probable.

The application of the steady-state method gives the following expression for the overall rate of the conversion of acetylene:

$$-\frac{d\left[C_{2}H_{2}\right]}{dt} = 2k_{1}\left[C_{2}H_{2}\right]\left(1 + \frac{k_{4}\left[C_{2}H_{2}\right]}{k_{4}\left[C_{2}H_{2}\right] + k_{7}}\right) \approx 4k_{1}\left[C_{2}H_{2}\right] \quad (11.11)$$

If it is assumed that  $k_7$  is substantially less (for the case of concentrated acetylene) than the product  $k_4$  [C<sub>2</sub>H<sub>2</sub>], then we have the first-order conversion of acetylene observed in practice.

The hydrogen added to acetylene in the glow discharge disso-

ciates intensively into atoms.

It may seem that the presence of atomic hydrogen must have increased the role of reaction 4, which would have led in the long run to an increase of the rate of decomposition of acetylene. Experiments, however, show the converse to be true. The point is probably that in the presence of a high concentration of hydrogen atoms the following reaction proceeds readily and rapidly:

(8) 
$$C_2H + H \longrightarrow C_2H_2$$

which regenerates acetylene. This reaction competes with reaction 5 which leads to the end products. In other words, there occurs the recombination of hydrogen atoms on acetylene.

Thus, according to the supposed mechanism, the conversion of acetylene diluted with hydrogen may be described by the following reactions:

(1) 
$$C_2H_2 \longrightarrow C_2H + H$$

$$(4) \quad C_2H_2 + H \longrightarrow C_2H + H_2$$

(8) 
$$C_2H + H \longrightarrow C_2H_2$$

$$(5) \quad C_2H + C_2H_2 \longrightarrow C_4H_3$$

(9) 
$$H_2 \longrightarrow 2H$$

(7) H 
$$\longrightarrow \frac{1}{2} H_2$$

Applying the steady-state method, we obtain the following expression for the rate of conversion of acetylene:

$$-\frac{d\left[C_{2}H_{2}\right]}{dt} = 4k_{5}\left[C_{2}H_{2}\right]^{2}\left[\frac{2k_{1}k_{4}\left[C_{2}H_{2}\right] + k_{1}k_{7} + k_{4}k_{9}\left[H_{2}\right]}{2k_{8}k_{9}\left[H_{2}\right] + 2k_{4}k_{5}\left[C_{2}H_{2}\right]^{2} + k_{5}k_{7}\left[C_{2}H_{2}\right]}\right]$$
(11.12)

At high concentrations of  $[H_2]$  the main part both in the numerator and in the denominator is played by the terms containing the hydrogen concentration; the remaining terms may be neglected. In this case, a second-order equation obtains:

$$-\frac{d\left[C_{2}H_{2}\right]}{dt} = \frac{2k_{5}k_{4}}{k_{8}}\left[C_{2}H_{2}\right]^{2}$$
(11.13)

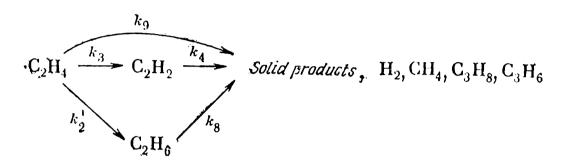
which is exactly observed in experiments.

The Kinetics of Conversion of Ethylene. This process has been studied at current values 32, 75, 125, 175, 225, and 350 mA. Figure 11.8 is a plot of the overall extent of conversion of ethylene versus the specific energy. As can be seen, the data for all the currents used lie on a single curve calculated by the first-order law [Eq. (11.10)] with an average value of the constant  $k_1 = 0.046$  litre/W·hr. Only the points that correspond to the lowest current (32 mA) deviate appreciably from the calculated curve.

The main gaseous product of the reaction is acetylene; apart from acetylene, there are also formed ethane, propane, propylene, and methane. A considerable polymerization of ethylene was also observed: from 10 per cent at low values of U/v to 80 per cent at high values of U/v.

As has been shown by a study of the kinetic curves, the best agreement with experiment is exhibited by the following kinetic

scheme of the reaction:



Taking into account the experimentally determined first order of the conversion of acetylene, ethylene, and ethane (see below), we write a system of equations for the rates of formation-decomposition of these hydrocarbons:

$$-\frac{d\left[C_{2}H_{4}\right]}{dt} = \left(k_{2}' + k_{3} + k_{9}\right)\left[C_{2}H_{4}\right]$$
 (11.14)

$$\frac{d \left[ C_2 H_2 \right]}{dt} = k_3 \left[ C_2 H_4 \right] - k_4 \left[ C_2 H_2 \right]$$
 (11.15)

$$\frac{d \left[ C_2 H_6 \right]}{dt} = k_2' \left[ C_2 H_4 \right] - k_8 \left[ C_2 H_6 \right]$$
 (11.16)

A solution of these simultaneous equations after appropriate rearrangements and the substitution of U/v for t yields the following expression for the extents of conversion:

$$1 - \Delta_{C_2 H_4} = e^{-a_3 \frac{U}{v}} \tag{11.17}$$

$$\gamma_{C_2H_2} = \frac{k_3}{a_4 - a_3} \left( e^{-a_3 \frac{U}{v}} - e^{-a_4 \frac{U}{v}} \right)$$
 (11.18)

$$\gamma_{C_2H_6} = \frac{k_2'}{a_3 - a_2} \left( e^{-a_2 \frac{U}{v}} - e^{-a_3 \frac{U}{v}} \right)$$
 (11.19)

where  $a_3 = k_3 + k_9 + k'_2$ ,  $a_4 = k_4$  and  $a_2 = k_8$  are the rate constants for the overall conversion of ethylene, acetylene, and ethane, respectively.

Figure 11.9 shows, as an example, the curves for a current of 125 mA, which have been calculated by Eqs. (11.17), (11.18) and (11.19) with the experimentally found constants:  $a_2 = 0.013$ ,

 $a_3 = 0.043$ , and  $a_4 = 0.030$  and also with the following values chosen:  $k_3 = 0.030$ ,  $k_9 = 0.009$ , and  $k'_2 = 0.004$ . As can be seen, the experimental data lie well on the calculated curves. Attempts to calculate other schemes, in particular, the scheme which does

not take into account the direct conversion of ethylene into the end products with the constant  $k_9$ , have failed to describe satisfactorily the experimentally obtained relations.

The Mechanism of Conversion of Ethylene in a Glow Discharge at a Low Pressure. In considering the values of the constants describing experimental data, one can see that the principal path in the decomposition of ethylene is the reaction of formation of acetylene. Besides, the overall conversion of ethylene proceeds by first-order kinetics. To this there corresponds the molecular pathway of formation of acetylene, the reactant molecules being activated by an electron impact:

(1) 
$$\begin{cases} C_2H_4 + \stackrel{\leftarrow}{e} \longrightarrow C_2H_4^* + e \\ C_2H_4^* \longrightarrow C_2H_2 + H_2 \end{cases}$$

We may suppose that the formation of ethane, which is described by a lower rate constant, takes place by way of a stepwise hydrogenation of ethylene by the atomic hydrogen resulting from the dissociation of hydrogen molecules or from any other process:

(2) 
$$C_2H_4 + H \longrightarrow C_2H_5$$

$$(3) \quad C_2H_5 + H \longrightarrow C_2H_6$$

As regards methane, because of the lack of experimental data it is difficult to say something definite about the mechanism of its formation. Evidently, the radicals CH3 which could be formed in the reaction

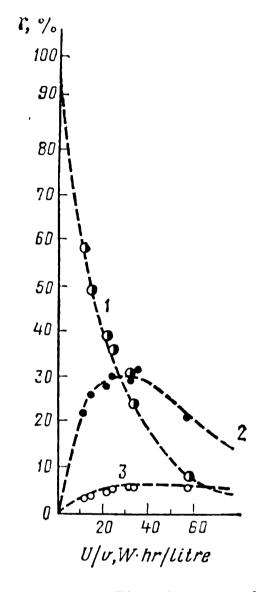


Fig. 11.9. The degrees of conversion of ethylene into the end products versus the specific energy (I = 125 mA). The curves have been calculated by the scheme given on page 314:

$$1-(1-\Delta_{C_2H_4});$$
  $2-\gamma_{C_2H_2};$   $3-\gamma_{C_2H_6}.$ 

$$(4) \quad H + C_2H_5 \longrightarrow 2CH_3$$

recombine further with atomic hydrogen, the molecules formed being stabilized at the wall since a triple collision is hardly probable under the conditions of our experiments.

The presence of propane and propylene in the cracking products can be explained by the following reactions:

(5) 
$$CH_3 + C_2H_5 \longrightarrow C_3H_8$$

(6) 
$$CH_3 + C_2H_3 \longrightarrow C_3H_6$$

The radical C<sub>2</sub>H<sub>3</sub> may result either from the direct dehydrogenation of the ethylene molecule excited by an electron impact

(7) 
$$C_2H_4^* \longrightarrow C_2H_3 + H$$

or from the reaction

(8) 
$$C_2H_4 + H \longrightarrow C_2H_3 + H_2$$

Besides, in considering the kinetic curves of  $\gamma_{C_3H_8}$  and  $\gamma_{C_3H_8}$  it may be supposed that propylene is formed by way of dehydrogenation of propane:

(9) 
$$C_3H_9 \longrightarrow C_3H_6 + H_2$$

Since in the zone of the glow discharge at low pressures there may take place the various energy conditions and the ethylene

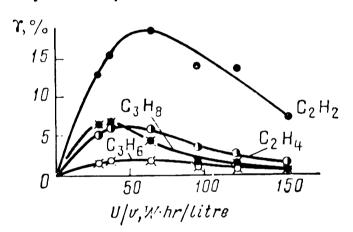


Fig. 11.10. The degrees of conversion of ethane into various products versus the specific energy; I = 350 mA.

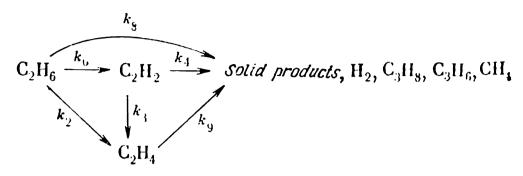
molecules may be activated not only by a collision with electrons possessing various energy reserves but also simply by thermal means, along with the above-indicated reactions there may also occur the molecular polymerization of ethylene by second-order kinetics.

The Kinetics of Conversion of Ethane. The kinetics of the conversion of ethane have been studied at the same current values: 32, 75, 125, 175, 225, and

350 mA. The major product here is also acetylene. Besides, there are formed methane, ethylene, propane, propylene, and also solid and resinous products. The degree of conversion of ethane in these reactions is several per cent in experiments with low current values and amounts to 70-80 per cent at high currents and degrees of overall conversion of 80-90 per cent.

Figure 11.10 presents the experimentally found dependences (at 350 mA) of the degrees of conversion  $\gamma$  of ethane to acetylene, ethylene, propane, and propylene on the specific energy. As can be seen, all  $\gamma$  pass with increasing U/v through a maximum. The dependence of the degree of overall conversion of ethane on the specific energy (not shown in Fig. 11.10) is expressed by two curves: one for high and the other for low currents. Thus, the function  $\Delta = f(U/v)$  is not unambiguous. Equation (11.10), which

is first order, is well justified at high current values. For a kinetic description of the conversion of ethane the following scheme has been established:



Setting up the rate equations by the first-order law for the formation-decomposition of ethane, ethylene, and acetylene [similar to Eqs. (11.3), (11.4), and (11.5)], and then integrating, we obtain the dependences of the degrees of conversion on U/v:

$$1 - \Delta_{\mathbf{C}_2 \mathbf{H}_c} = e^{-a_z \frac{U}{v}} \tag{11.20}$$

$$\gamma_{C_2 1 I_4} = \frac{k_2}{a_3 - a_2} \left( e^{-a_3 \cdot \frac{U}{v}} - e^{-a_3 \cdot \frac{U}{v}} \right) \tag{11.21}$$

$$\gamma_{C_2H_2} = k_6 \left[ \frac{b_0 - a_2}{(a_3 - a_2)(a_4 - a_2)} e^{-a_2 \frac{U}{v}} - \frac{b_0 - a_3}{(a_3 - a_2)(a_4 - a_3)} e^{-a_4 \frac{U}{v}} + \frac{b_0 - a_4}{(a_4 - a_2)(a_4 - a_3)} e^{-a_4 \frac{U}{v}} \right]$$
(11.22)

in which  $a_2$ ,  $a_3$ , and  $a_4$  are the constants of the overall conversion of ethane, ethylene, and acetylene, and

$$b_0 = a_3 + \frac{k_2 k_3}{k_5}$$

In calculations by means of formulas (11.20), (11.21), and (11.22) use has been made of the experimental values of  $a_2$  and  $a_3$ ,  $a_4$ ;  $k_3$  and  $k_9$  are taken from the calculations of the decomposition of ethylene, and the values of  $k_2$ ,  $k_6$ , and  $k_8$  are chosen so that their sum is equal to the experimental value of  $a_2$ .

As seen from Fig. 11.11, the curves calculated, as an example, for 350 mA are in good agreement with the experimental points. The curves shown in Fig. 11.11 have been calculated by using the following values:

$$a_2 = k_2 + k_3 + k_8 = 0.018;$$
  $a_3 = k_3 + k_9 = 0.05;$   $k_4 = a_4 = 0.02;$   $k_2 = 0.005;$   $k_6 = 0.006;$   $k_8 = 0.007;$   $k_7 = 0.03$  and  $k_9 = 0.02$  litre/W·hr

Calculations have been carried out according to other schemes as well, in particular, according to the scheme in which acetylene is entirely formed from ethane via the intermediate formation of ethylene ( $k_6 = 0$ ). However, no matter what values of the constants were taken (except the negative values) no agreement

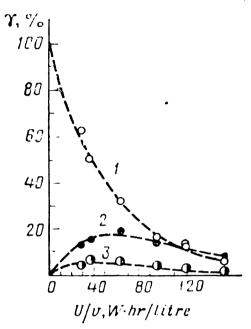


Fig. 11.11. The degrees of conversion of ethane into the end products versus specific energy (I = 350 mA):

 $I-(1-\Delta_{C_2H_6})$ ;  $2-\gamma_{C_2H_2}$ ;  $3-\gamma_{C_2H_4}$ . The curves have been calculated by the scheme given on page 317.

with the experimental data could be achieved. The calculations of the scheme without the constant  $k_8$  have failed either. Therefore we may presume that the above-given scheme reflects the actual sequence of consecutive-parallel reactions of conversion of hydrocarbons in the decomposition of ethane in the electrical discharge.

Discussion of the Mechanism of Conversion of Ethane. The following activation processes taking place on collisions with electrons are thought to be the most natural:

(1) 
$$C_2H_6 + e \longrightarrow 2CH_3 + e$$
  
 $\Delta H = 86 \pm 2 \text{ kcal/mole}$ 

(2) 
$$C_2H_6 + \stackrel{\leftarrow}{e} \longrightarrow C_2H_5 + H + e$$
  
 $\Delta H = 97 \pm 1 \text{ kcal/mole}$ 

The atomic hydrogen and the radical CH<sub>3</sub> resulting from these reactions interact with the starting ethane molecules:

(3) 
$$H + C_2H_3 \longrightarrow C_2H_5 + H_2$$

(4) 
$$CH_3 + C_2H_6 \longrightarrow C_2H_5 + CH_4$$

which again give rise to ethyl radicals and methane, the latter being found among the reaction products. The activation energies of reactions 3 and 4 do not exceed 8 kcal/mole according to the data obtained by Steacie.

The formation of ethylene may occur as a result of the further excitation of the ethyl radical in the discharge and its decomposition according to the equation

(5) 
$$C_2H_5 + \stackrel{\leftarrow}{e} \longrightarrow C_2H_4 + H + e$$

The heat of this reaction is about 40 kcal/mole, and the energy of activation does not probably exceed 43 kcal/mole. The possibility is not excluded that the ethylene can be formed by the molecular dehydrogenation of ethane:

(6) 
$$C_2H_6 \longrightarrow C_2H_4 + H_2$$

which has been noted by some authors who have studied the thermal decomposition of this compound.

The "direct" formation of acetylene is possible by the following

reactions:

(7) 
$$C_2H_5 + \stackrel{\leftarrow}{e} \longrightarrow C_2H_3 + H_2 + e$$

(8) 
$$C_2H_3 + \stackrel{\leftarrow}{e} \longrightarrow C_2H_2 + H + e$$

the preceding activation of the radicals taking place as a result of electron impacts.

Neglecting all the reactions involving two radicals because of their small concentrations as compared with the starting ethane and taking into account the recombination of hydrogen on the wall, we obtain a series of reactions describing the mechanism of the conversion of ethane:

$$C_{2}H_{6} + \stackrel{\leftarrow}{e} \xrightarrow{k_{1}} 2CH_{3} + e$$

$$C_{2}H_{6} + \stackrel{\leftarrow}{e} \xrightarrow{k_{2}} C_{2}H_{5} + H + e$$

$$H + C_{2}H_{6} \xrightarrow{k_{3}} C_{2}H_{5} + H_{2}$$

$$CH_{3} + C_{2}H_{6} \xrightarrow{k_{4}} C_{2}H_{5} + CH_{4}$$

$$C_{2}H_{5} + \stackrel{\leftarrow}{e} \xrightarrow{k_{5}} C_{2}H_{4} + H + e$$

$$C_{2}H_{5} + \stackrel{\leftarrow}{e} \xrightarrow{k_{3}} C_{2}H_{3} + H_{2} + e$$

$$C_{2}H_{3} + \stackrel{\leftarrow}{e} \xrightarrow{k_{9}} C_{2}H_{2} + H + e$$

$$H \xrightarrow{k_{14}} \frac{1}{2}H_{2}$$

The main part in this mechanism is played by the activation of molecules and radicals by an electron impact with the subsequent decomposition of the excited particles. The application of the steady-state principle to the reactions listed gives the following simple expression for the rate of decomposition of ethane:

$$-\frac{d\left[C_{2}H_{6}\right]}{dt} = (3k_{1} + k_{2})\left[C_{2}H_{6}\right] + 2k_{3}\frac{k_{1} + k_{2}}{k_{14}}\left[C_{2}H_{6}\right]^{2}$$

Thus, depending on the reaction conditions, the reaction may proceed either by first-order or second-order kinetics.

The Kinetics of Conversion of Methane. The kinetics of the conversion of methane have also been studied at current values 32, 75, 125, 175, 225, and 350 mA. Experiments have been carried out at low (1.2-1.3 mm Hg) and higher pressures (about 3 mm Hg). The major products of the conversion of methane are ethane, acetylene, ethylene, propane, propylene, and solid substances.

Figure 11.12 shows the curves of the degree of conversion  $\gamma$  of methane to the various products versus the specific energy, which have been obtained at a current of 225 mA. The principal conclusion following from this graph and those similar to it at other current values consists in that the main gaseous product of the conversion of methane is ethane. The  $\gamma_{C_2H_6}$  curves pass through a maximum with increasing specific energy; the position of the maximum shifts with decreasing current to the side of large U/v, and its height increases, reaching the value  $\gamma=23$ 

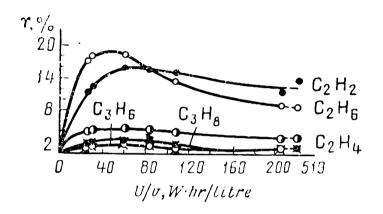


Fig. 11.12. The degrees of conversion of methane into the end products versus specific energy (P = 1.2-1.3 mm Hg, I = 225 mA).

per cent. Thus, under the conditions studied one-fourth of the starting methane is converted into ethane. Acetylene is only second in importance. The degrees of conversion to acetylene,  $\gamma_{C_9H_9}$ , versus the ratio U/v also pass through a maximum, but in contrast to ethane, the maximum yields increase with increasing current strength. The highest value of  $\gamma_{C_0H_0}$  under these

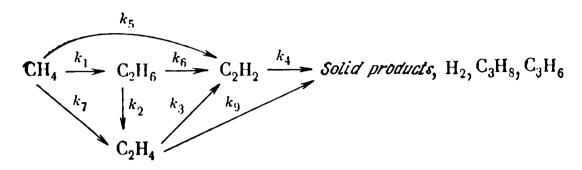
conditions does not, however, exceed 16 per cent. Nonetheless, with increasing current, i.e., the discharge power, there is a tendency for the ratio to change to the side of predomination of the acetylene yield. This observation has also been confirmed by experiments carried out at a pressure of 3 mm Hg. Here, with equal current values the voltage on the electrodes increases considerably, and so does the discharge power. The main product is acetylene. As known, at still higher pressures (28-36 mm Hg) ethane does not practically appear among the reaction products. Returning to Fig. 11.12, we note that the amount of ethylene in the reaction products is much less than that of ethane and acetylene. The height of the maximum of the curve of  $\gamma_{C_2H_4}$  versus f(U/v) falls from 4.5 per cent at 350 mA down to 1.7 per cent at 32 mA.

Thus, the conditions studied are favourable for the formation of ethane. It may seem that at least here the kinetic scheme of consecutive conversions is realized:

$$CH_4 \implies C_2H_6 \implies C_2H_4 \implies C_2H_2 \implies C+H$$

which was proposed by Kassel in 1930 and has been used in a number of works up to the present time. But actually this is not so. Even a comparison of the yields of ethane and ethylene confirms the possibility of their independent formation. Attempts

to describe in detail the dependences of the degrees of conversion of methane to the main products on the specific energy lead to the following scheme of consecutive and parallel reactions:



Methane reacts, according to the same scheme, in three parallel directions: the conversion to ethane  $(k_1)$  and the "direct" conversions, i.e., without the formation of stable intermediate products, to ethylene  $(k_7)$  and acetylene  $(k_5)$ . The conversions of the resulting ethylene, ethane, and acetylene formed are supposed to be analogous to the conversions described earlier in the kinetic schemes established for the reactions of these hydrocarbons.

Assuming the kinetic first order for all the reactions, we write equations for the reaction rates:

$$-\frac{d [CH_4]}{dt} = (k_1 + k_5 + k_7) [CH_4]$$
 (11.23)

$$\frac{d \left[ C_2 H_6 \right]}{dt} = \frac{1}{2} k_1 \left[ CH_4 \right] - (k_2 + k_6) \left[ C_2 H_6 \right]$$
 (11.24)

$$\frac{d\left[C_{2}H_{4}\right]}{dt} = \frac{1}{2} k_{7} \left[CH_{4}\right] + k_{2} \left[C_{2}H_{6}\right] - (k_{3} + k_{9}) \left[C_{2}H_{4}\right]$$
(11.25)

$$\frac{d\left[C_{2}H_{2}\right]}{dt} = \frac{1}{2} k_{5} \left[CH_{4}\right] + k_{6} \left[C_{2}H_{6}\right] + k_{3} \left[C_{2}H_{4}\right] - k_{4} \left[C_{2}H_{2}\right] \dots (11.26)$$

The solution of this system of equations gives (upon replacement of t by U/v) the following expressions for the degrees of conversion of the hydrocarbons:

$$1 - \Delta_{\text{CH}_4} = e^{-a_1 \frac{U}{y}} \tag{11.27}$$

$$\gamma_{C_2H_6} = \frac{1}{2} \frac{k_1}{a_2 - a_1} \left( e^{-a_1 \frac{U}{v}} - e^{-a_2 \frac{U}{v}} \right)$$
 (11.28)

$$\gamma_{C_2H_4} = \frac{1}{2} k_7 \left( \frac{b_0 - a_1}{(a_2 - a_1)(a_3 - a_1)} e^{-a_1 \frac{U}{v}} + \frac{b_0 - a_2}{(a_1 - a_2)(a_3 - a_2)} e^{-a_1 \frac{U}{v}} + \right)$$

$$+\frac{b_0-a_3}{(a_1-a_3)(a_2-a_3)}e^{-a_1}\frac{U}{v}$$
(11.29)

$$\gamma_{C_2H_2} = \frac{1}{2} k_5 \left( \frac{a_1^2 - a_1b_1 + b_2}{(a_2 - a_1)(a_3 - a_1)(a_4 - a_1)} e^{-a_1 \frac{U}{v}} + \frac{a_2^2 - a_2b_1 + b_2}{(a_1 - a_2)(a_3 - a_2)(a_4 - a_2)} e^{-a_2 \frac{U}{v}} + \frac{a_3^2 - a_3b_1 + b_2}{(a_1 - a_3)(a_2 - a_3)(a_4 - a_3)} e^{-a_1 \frac{U}{v}} + \frac{a_4^2 - a_4b_1 + b_2}{(a_1 - a_4)(a_2 - a_4)(a_3 - a_4)} e^{-a_4 \frac{U}{v}} \right)$$
(11.30)

Here the following notations are used for the rate constants of the overall conversion of methane, ethane, ethylene, and acetylene:

$$a_1 = k_1 + k_5 + k_7$$
,  $a_2 = k_2 + k_6$ ,  
 $a_3 = k_3 + k_9$  and  $a_4 = k_4$ , and  $b_0 = a_2 + \frac{k_1 k_2}{k_7}$ ,  
 $b_1 = a_2 + a_3 + \frac{k_1 k_6 + k_3 k_7}{k_5}$ ,  $b_2 = a_2 a_3 + \frac{k_1 k_6 a_2 + k_3 k_7 b_0}{k_5}$ 

Formulas (11.27), (11.29), and (11.30) have been used to calculate the curves of the disappearance of methane and the varia-

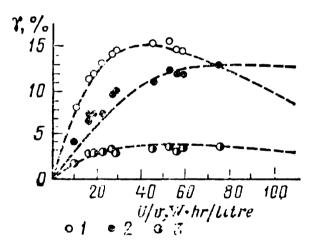


Fig. 11.13. The degrees of conversion of methane into the end products against the specific energy:  $1-\gamma_{C_2H_6}$ ;  $2-\gamma_{C_2H_2}$ ;  $3-\gamma_{C_2H_6}$ . The dotted curves have been calculated according to the scheme given on page 321.

tion of the degree of its conversion versus the specific energy U/v. An example of the calculations made is given in Fig. 11.13. The values of the constants used are presented in Table 11.1.

As can be seen from Fig. 11.13, the calculated curves agree quite satisfactorily with the experimental data.

Attempts have also been made to calculate other schemes of conversion of methane (in particular, the Kassel consecutive scheme), schemes that do not involve  $k_5$ ,  $k_7$ , or  $k_6$ . But, no matter what values of the constants were the experimental and calculated

used, no agreement between curves could be achieved.

Thus, under the conditions studied there exist 4 paths for the formation of acetylene from methane:

- (1) "directly" from methane (with the constant  $k_5$ );
- (2) via ethane, no ethylene being formed (with the constants  $k_1$  and  $k_6$ ),
  - (3) from ethylene formed "directly" from methane  $(k_7 \text{ and } k_3)$ ;
  - (4) via ethane and ethylene as intermediates  $(k_1, k_2, \text{ and } k_3)$ .

The calculations of  $\gamma_{C_2H_2}$  carried out by means of formulas corresponding to each of these paths, are presented in Fig. 11.14. As seen, the major part of acetylene in the electrocracking of methane even under the conditions favourable for the formation

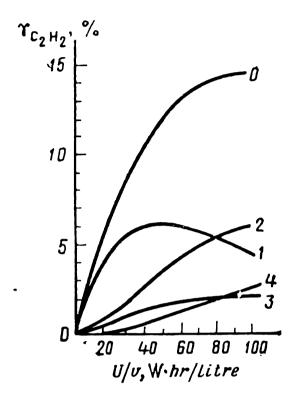


Fig. 11.14. Comparison of the various paths of formation of acetylene from methane by their contribution to the total degree of conversion into acetylene: 0—the total curve according to the scheme given on page 321:

$$1-CH_{4} \xrightarrow{k_{5}} C_{2}H_{2} \xrightarrow{k_{4}} ; 2-CH_{4} \xrightarrow{k_{1}} C_{2}H_{6} \xrightarrow{k_{6}} C_{2}H_{2} \xrightarrow{k_{4}} ; 3-CH_{4} \xrightarrow{k_{7}} C_{2}H_{4} \xrightarrow{k_{8}} C_{2}H_{2} \xrightarrow{k_{4}}$$

$$4-CH_{4} \xrightarrow{k_{1}} C_{2}H_{6} \xrightarrow{k} C_{2}H_{4} \xrightarrow{k_{3}} C_{2}H_{2} \xrightarrow{k_{4}}$$

TABLE 11.1. The Kinetic Constants (litre/W·hr) Found for Reactions of Conversion of Methane in the Glow Discharge at Low Pressure

Notation for constants	at $I = 225$ mA; p = 1-2 mm Hg	at $I = 350 \text{ mA};$ p = 3  mm Hg
$a_1 = k_1 + k_5 + k_7$	0.028	0.044
$k_1$	0.0185	0.021
$k_5$	0.006 .	0.016
k <sub>7</sub>	0.0035	0.007
$a_2 = k_2 + k_6$	0.018	0.009
$k_2$	0.008	0.005
$k_6$	0.010	0.004
$a_3 = k_3 + k_9$	0.040	0.020
$k_3$	0.030	0.020
$k_9$	0.010	0.000
$a_4 = k_4$	0.020	0.004

of ethane, is formed by the first pathway which is probably associated only with unstable intermediates of the type of radicals or ions. Of somewhat lesser importance are the second and third paths and only a small proportion of acetylene, about one-tenth, is formed, even under the "mild" conditions studied, by the Kassel consecutive scheme, i.e., via ethane and ethylene. From the data obtained it also follows that under more "severe" conditions at increased pressures and current values the ratio of the rate constants in the scheme (page 321) varies in such a manner that the consecutive scheme becomes unimportant and the radical processes of "direct" conversion of methane to acetylene begin to play the dominant part.

## 11.4. Synthesis of Nitric Oxide from Air and Nitrogen-Oxygen Mixtures. Decomposition of Nitric Oxide

The kinetics of the reversible reaction

$$N_2 + O_2 \implies 2NO$$

in an electrical discharge was first studied by Vasiliev, Kobozev, and Yeremin.

The derivation of the basic equation may be given as follows. Let x be the concentration of nitric oxide; the slightly varying concentrations of nitrogen and oxygen are included in the constant  $k_1$  because of their smallness;  $\gamma$  is the kinetic order of the decomposition of nitric oxide. Then

$$\frac{dx}{dt} = k_1 U - k_2 U x^{\mathsf{Y}} \tag{11.31}$$

Experiment shows that in most cases the first order of the decomposition of NO is better justified, i.e.,  $\gamma = 1$ ; in other cases  $\gamma = 2$  is more consistent with experimental data. On the assumption of second order the integration of Eq. (11.31) at constant power U leads to the following result:

$$k_2 U t = \frac{1}{2 \left(\frac{k_1}{k_2}\right)^{1/2}} \ln \frac{\left(\frac{k_1}{k_2}\right)^{1/2} + x}{\left(\frac{k_1}{k_2}\right)^{1/2} - x}$$
(11.32)

or

$$x = \left(\frac{k_1}{k_2}\right)^{1/2} \cdot \frac{1 - e^{-2(k_1 k_2)^{1/2} Ut}}{1 + e^{-2(k_1 k_2)^{1/2} Ut}}$$
(11.33)

Replacing, as before, the reaction time t in Eq. (11.33) by 1/v (hr/litre), we finally get

$$x = \left(\frac{k_1}{k_2}\right)^{1/2} \cdot \frac{1 - e^{-2(k_1 k_2)^{1/2}} \frac{U}{v}}{1 + e^{-2(k_1 k_2)^{1/2}} \frac{U}{v}} = \% \text{ NO}$$
 (11.34)

This equation is consistent with the limiting conditions that characterize the experimentally found dependence of the percentage of nitric oxide on the specific energy. Indeed, for the case where  $U/v \rightarrow \infty$  we have

$$(\% \text{ NO})_{\infty} = x_{\infty} = \left(\frac{k_1}{k_2}\right)^{1/2}$$
 (11.35)

that is, a stationary state is attained, which is characterized for the curves I and 3 in Fig. 11.15 by the values 11.4 and 8.3 vol.

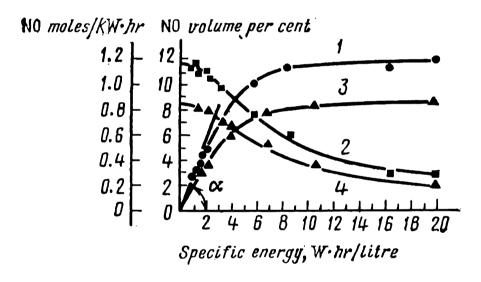


Fig. 11.15. The dependence of the concentration of nitric oxide (curves 1 and 3) and of the energy yield (curves 2 and 4) on specific energy.

per cent of NO. It can be shown that at low specific energies x is approximately equal to  $k_1(U/v)$ , i.e., is proportional to U/v according to Fig. 11.15. To calculate the constants, it is necessary to know at least two points of the curve. The steady-state concentration gives, in accordance with expression (11.35), the ratio  $k_1 k_2$ . Substituting this ratio into formula (11.34) and using the known concentration at any intermediate value of U/v, we find  $k_2$ . Thus, for the data of Fig. 11.15 the following values have been obtained, on an average,

Composition of the original mixture	$k_1$	$k_2$
50 vol. $\% O_2 + 50$ vol. $\% N_2$	2.58	0.0199
Air	1.88	0.0273

It is these values of the constants that have been used to calculate the curves of Fig. 11.15, which agree satisfactorily with the

experimental points. The curves 2 and 4 showing the dependence of the energy yield on the specific energy were calculated from the relation

$$\alpha = \frac{x}{2.24 \left(\frac{U}{v}\right)} \text{ moles NO/kW · hr}$$
 (11.36)

It should be noted that the values of the constants and steady-state concentrations of nitric oxide given here are characteristic only of the given experimental conditions. Under other conditions there may be obtained other values. For instance, in a wider discharge tube the stationary concentrations, i.e., the values of  $(k_1/k_2)^{1/2}$ , are smaller. This is probably indicative of the great part played by heterogeneous processes in a narrow discharge tube. Besides, the stationary concentrations of NO depend on the pressure and the current strength.

Likewise, as has already been mentioned, the decomposition of nitric oxide in an electrical discharge proceeds more frequently by first-order kinetics. In this case, integration of Eq. (11.31) leads to the following relation (after the replacement of t by 1/v):

$$x = \frac{k_1}{k_2} \left( 1 - e^{-k_2 \frac{U}{v}} \right) \tag{11.37}$$

In limiting cases at  $(U/v) \rightarrow \infty$ 

$$x = \frac{k_1}{k_2} \tag{11.38}$$

and at  $U/v \rightarrow 0$ 

$$x = k_1 \frac{U}{v} \tag{11.39}$$

that is, to large specific energies there corresponds the limiting concentration of nitric oxide.

In the initial region, however, there exists a proportional relation.

## 11.5. Mechanism of Activation of Molecules in an Electrical Discharge

The specificity of the chemical action of electrical discharges is first of all accounted for by the fact that the energy supplied to the discharge is concentrated in the electron gas in the initial stage of its transformation. Here, because of the large difference in mass between electrons and molecules, the energy transfer from electrons to molecules by means of elastic collisions occurs slowly. Therefore, the average energy of electrons may be considerably higher than the average energy of neutral molecules

and heavy ions. This difference between the average energies is sometimes characterized by ascribing unequal temperatures to electron and molecular gases, which is valid on the condition of the applicability of the Maxwell-Boltzmann distribution law to the electron gas. When the electron "temperature" is substantially higher than the molecular "temperature", we speak of the non-isothermal plasma of the discharge in which there exist conditions for the formation of the superequilibrium concentrations of the reaction products. An example is the formation of nitric oxide in

concentrations of up to 11 vol. per cent (see Sec. 11.4), which are about twice as high as the maximum possible thermodynamic equilibrium concentrations.\*

The energy of the electron gas is transmitted on collisions between electrons and molecules, during which the latter are excited, ionized, and dissociated.

It may be thought that the direct dissociation of molecules on collisions with electrons and the appearance of highly chemically active free atoms and radicals plays an important part during reactions in an electrical discharge, especially at low pressures. Thus, the mechanism of dissociation of hydrogen illustrated in Fig. 11.16 is believed to be very probable. An electron impact \*\*

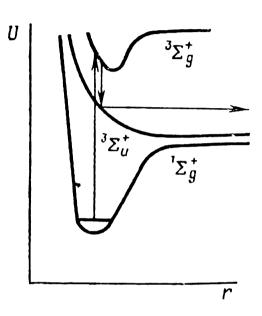


Fig. 11.16. The dissociation of hydrogen into normal atoms upon an electron impact.

induces the electronic excitation of the molecule, which passes from the ground singlet state  $^{1}\Sigma_{g}^{+}$  to the triplet state  $^{3}\Sigma_{g}^{+}$ . For this to occur, an electron must have a minimum energy of the order of 11.4 eV, which corresponds to the "temperature" 85,000 K. Since the reverse spontaneous transition is forbidden, there takes place an allowed transition of the molecule from the high level to the unstable state  $^{3}\Sigma_{u}^{+}$  and then the molecule dissociates into normal atoms and radiates an excess energy. Thus, for example, in a glow discharge at a low pressure and an average molecular temperature (about 800°), the degree of dissociation of hydrogen may reach stationary values close to unity. The equilibrium degree of dissociation of hydrogen is about  $10^{-10}$  at 800 K. The process

<sup>\*</sup> As the temperature mounts the equilibrium concentration of nitric oxide formed according to the equation  $N_2 + O_2 \rightleftharpoons 2NO$  passes through a maximum due to the dissociation of  $O_2$  and  $N_2$ .

<sup>\*\*</sup> Quantum restrictions — the selection rules — are not so strictly observed on electron impacts as in the absorption and emission of light.

of dissociation may be schematically represented by the following equation:

$$H_2 + \stackrel{\leftarrow}{e} \longrightarrow H + H + e$$

It may be supposed that a similar or closely related mechanism of "electronic activation" plays an important part in many cases. A direct indication is the kinetic first order which is observed in the diverse reactions taking place in electrical discharges. For instance, in the above-considered mechanisms of the conversion of hydrocarbons in a glow discharge at low pressures the slowest rate-controlling processes are the following reactions:

$$C_{2}H_{2} + \stackrel{\leftarrow}{e} \longrightarrow C_{2}H + H + e$$

$$C_{2}H_{4} + \stackrel{\leftarrow}{e} \longrightarrow C_{2}H_{2} + H_{2} + e$$

$$C_{2}H_{6} + \stackrel{\leftarrow}{e} \longrightarrow 2CH_{3} + e$$

$$C_{2}H_{6} + \stackrel{\leftarrow}{e} \longrightarrow C_{2}H_{5} + H + e$$

The dissociation caused by an electron impact is also supposed to occur in the synthesis of ozone:

$$O_2 + e \longrightarrow 2O + e$$

and in the synthesis of hydrogen peroxide. However, this is not the only plausible mechanism of the chemical activation of molecules by the electron gas. At higher pressures there becomes probable a collision between electronically excited and normal molecules and an energy transfer by a collision of the second kind, which is accompanied by the generation of a vibrationally excited molecule or even by its complete dissociation. The mechanism under discussion may be represented schematically as follows:

$$A_{2} + \stackrel{\leftarrow}{e} \longrightarrow A_{2}^{*} + e$$

$$A_{2}^{*} + B_{2} \longrightarrow A_{2} + B \iff B$$

$$A_{2}^{*} + B_{2} \longrightarrow A_{2} + B + B$$

or

Here  $A_2^*$  is an electronically excited molecule;  $B \longleftrightarrow B$  is a vibrationally excited molecule.

The above scheme forms the basis for the "energy catalysis" in an electrical discharge proposed as an activation mechanism in the work by Kobozev, Vasiliev and Yeremin mentioned above. As an example of the energy transfer by a collision of the

As an example of the energy transfer by a collision of the second kind may be cited the process that occurs in an electrical discharge in a mixture of argon and oxygen:

$$Ar^{\bullet}(^{3}P) + O_{2}(^{3}\Sigma) \longrightarrow Ar(^{1}S) + O(^{1}D) + O(^{1}S)$$

when on collision with excited argon the oxygen molecule dissociates into the atoms. It is also known that the presence of mercury vapour sensitizes the dissociation of hydrogen molecules on electron impacts. For instance, in the absence of mercury, the dissociation is noticeable only with electron energies not less than 11.4 eV, and in the presence of mercury at 7.7 eV. This is accounted for by the following sequence of processes:

$$e (7.7 \text{ eV}) + \text{Hg } (6 \, {}^{2}S_{1}) \longrightarrow \text{Hg } (7 \, {}^{3}S_{1}) + e (0 \text{ eV})$$
 $\text{Hg } (7 \, {}^{3}S_{1}) \longrightarrow \text{Hg } (6 \, {}^{3}P_{0}^{0}) + h\nu (4047 \text{Å or } 3.06 \text{ eV})$ 
 $\text{Hg } (6 \, {}^{3}P_{0}^{0}) (4.64 \text{ eV}) + \text{H}_{2} ({}^{1}\Sigma_{g}^{+}) \longrightarrow 2\text{H} + \text{Hg } ({}^{1}S_{0})$ 

The metastable mercury atom in the state  $6^3P_0^0$ , which is formed in the second stage and which has an excitation energy of 4.64 eV, spends its energy at the third stage on the dissociation of the molecule. This mechanism is similar, to a certain extent, to the mechanism of dissociation of hydrogen by photosensitized mercury in the known experiments accomplished by Franck and Cario.

Other experimental evidence for the theory of energy catalysis is furnished by spectroscopic investigations and also by the sensitizing effect of various added substances in reactions occurring in electrical discharges. For instance, a considerable increase of the yield of acetylene has been observed in the electrocracking of methane in a glow discharge in the presence of mercury vapour. The mechanism of such a "catalytic" action of mercury vapour consists probably of the primary formation of a metastable mercury atom and the subsequent sensitized dissociation of the methane molecule:

$$Hg\left(6^{3}P_{0}^{0}\right) + CH_{4} \longrightarrow CH_{3} + H + Hg\left(^{1}S_{0}\right)$$

There has also been studied the action of mercury and sodium vapours on the decomposition of ammonia in a glow discharge and also of mercury, zinc, and cadmium vapours on the synthesis of NH<sub>3</sub> from nitrogen and hydrogen. As has been found, the sensitizing effect is exhibited in both cases by mercury vapour alone, the decisive role being also attributed here to the metastable mercury atom (which is designated by the symbol Hg\*). The first stage of the sensitized decomposition of ammonia is represented by the equation

$$Hg^* + NH_3 \longrightarrow NH_2 + H + Hg$$

The synthesis of ammonia is supposed to take place by the interaction between the excited nitrogen molecule  $N_2^*$  and hydrogen atoms and the role of mercury is to sensitize the formation of the

hydrogen atoms. On the whole, the process in the presence of mercury is represented by the scheme

$$Hg + e \longrightarrow Hg^* + e \longrightarrow N_2^* + e \longrightarrow N_2^* + e \longrightarrow Hg^* + H_2 \longrightarrow HI + H + Hg \longrightarrow Hg^* + H \longrightarrow NH + N \longrightarrow NH + H_2 \longrightarrow NH_3 \longrightarrow NH + H_2 \longrightarrow NH + H, etc.$$

It is interesting to consider one more case of the positive effect of the substance added on the reaction in an electrical discharge, namely, the increase of the equilibrium-stationary yields of ozone in the presence of nitrogen. Here the role of the energy catalyst is apparently played by an electronically excited nitrogen molecule in the metastable state,  $N_2^*$ , which imparts its energy to the oxygen molecule by way of a collision of the second kind:

$$N_2^* + O_2 \longrightarrow O + O + N_2$$

We know also of the activating effect of argon and water vapour on the reaction of formation of hydrogen peroxide in a barrier discharge. These added substances probably also serve as energy catalysts and exert an influence on the dissociation of hydrogen molecules.

Thus, according to the theory of energy catalysis, a considerable part in the formation of chemically active particles in an electrical discharge (or free atoms in the examples given above) can be played by electronically excited atoms and molecules, mainly those which are perhaps in the metastable state. The analogy with catalysis consists here in that the particles in electronically excited states do not directly participate in the act of chemical interaction but serve only as agents that transfer energy from the electron gas of the discharge plasma to the molecules to be activated, thereby facilitating the formation of activated states. The difference from ordinary catalysis consists in the attainment of higher equilibrium (equilibrium-stationary) concentrations of the reaction products under the action of energy catalysts. In the above examples the role of energy catalysts is played by atoms and molecules of the substance added. This is evidently not obligatory. The analogous function can also be fulfilled by the electronically excited states of the reaction participants themselves, which transfer energy by means of collisions of the second kind to similar molecules or to the molecules of the other participants of the reaction. For example, in the synthesis of ammonia the following process is thought to be probable:

$$N_2^* + H_2 \longrightarrow N_2 + H + H$$

in which the role of an energy catalyst is played by a nitrogen molecule. As has already been pointed out, the extreme degree of activation which manifests itself in the dissociation into atoms is not evidently necessary in all cases either. In other cases, on collisions of the second kind, and also by other means, there may appear molecules in a state close to dissociation, i.e., at high levels of vibrational excitation. Such molecules can also be chemically active. For instance, in the oxidation of nitrogen the following reaction is regarded as an activation process:

$$N_2^* + N_2 \longrightarrow N_2 + N \longleftrightarrow N$$

in which the electron energy of one nitrogen molecule  $N_2^*$  is converted into the vibrational energy of another nitrogen molecule,  $N \longleftrightarrow N$ .

# Kinetics of Reactions in Solution

### 12.1. Effect of Solvents on the Rate of Chemical Reactions

Of considerable interest is a comparative study of the rates of a single reaction in the gas phase and in various solvents. The number of reactions that can be studied both in a gaseous medium and in solutions is not very large, but such reactions do exist and the decomposition of nitrogen pentoxide is one of the most thoroughly studied reactions of this kind:

$$N_2O_5 \longrightarrow N_2O_4 + \frac{1}{2}O_2$$

This reaction is a classical example of unimolecular reactions. Table 12.1 lists some data indicating the very slight effect of solvent on the rate of this reaction.

TABLE 12.1. The Constants of the Arrhenius Equation for the Decomposition of Nitrogen Pentoxide in the Gas Phase and in Various Solvents at 20 °C

	Arrhenius	Arrhenius constants		
Solvent	A, $\sec^{-1} \cdot 10^{-13}$	E, cal/mole	k <sub>gas</sub>	
Gas phase	4.5	24,500	1.00	
Carbon tetrachloride	2.8	24,100	1.24	
Chloroform	6.4	24,60C	1.45	
CH <sub>2</sub> ClCH <sub>2</sub> Cl	4.1	24,400	1.26	
CHCl <sub>2</sub> CHCl <sub>2</sub>	10.4	24,100	1.24	
CH <sub>3</sub> CHCl <sub>2</sub>	12.5	24,900	1.70	
$Br_2$	2.5	24,000	1.14	
CH <sub>3</sub> NO <sub>2</sub>	3.1	24,500	0.81	
$N_2O_4$	16.3	25,000	1.82	

For a chemically inert solvent this could have been expected if it is thought that the role of solvent molecules reduces to that of maintaining the Maxwell-Boltzmann distribution and, hence,

of the thermodynamic equilibrium concentration of active molecules. However, in certain other solvents—nitric acid and dichloropropane—nitrogen pentoxide decomposes by about 25 times more slowly and the energy of activation increases up to about 28,300 cal/mole. It is possible that in these solvents the molecules form with the solvents some complexes which stabilize the pentoxide to a certain extent. In a solution of  $N_2O_4$ , however, a somewhat greater rate seems to be observed (Table 12.1).

As a further example of the slight effect of solvent on the reaction rate may be cited the data on the decomposition of chlorine monoxide:

$$2Cl_2O \longrightarrow 2Cl_2 + O_2$$

Generally speaking, the kinetics of this process are rather complicated: at the beginning the reaction proceeds slowly and then is speeded up, the both stages proceeding by second-order kinetics with the same energy of activation. Table 12.2 compares the rates of this reaction in the gas phase and in a solution of carbon tetrachloride.

Properly speaking, because of certain difficulties in the determination of the rate constants it is the time periods required for the increase of the degree of conversion of  $Cl_2O$  from 20 to 60 per cent that are compared. Within the experimental error the rates in solution and in the gas phase coincide. The ratio  $\tau_{\text{solution}}/\tau_{\text{gas}}$  is equal, on an average, to 1.02. The energies of activation  $E_{\text{solution}}$  and  $E_{\text{gas}}$  are equal, respectively, to 20,300 and 21,000 cal/mole, i.e., they also almost coincide. However, the solvent can often be found to exert a considerable effect. For instance,

TABLE 12.2. Comparison of the Rates of the Reaction  $2Cl_2O \rightarrow 2Cl_2 + O_2$  in the Gas Phase and in Carbon Tetrachloride Solution

Concentration		$ au_{20-60\%}$ , min		τ <sub>solution</sub>
of Cl₂O, mole/litre	of Cl <sub>2</sub> O, t, °C —	in solution	in gas	tgas
0.224	70.7	50	47.5	1.05
0.115	71.0	105	90.5	1.16
0.115	59.8	257	225	1.14
0.126	69.8	83	90.5	0.92
0.095	69.7	100	122	0.82
0.120	80.1	55	44	1.25
0.120	75.3	54	61	0.89
0.120	65.2	139	137	1.02
0.120	60.1	200	211	0.95

ozone in the gas phase decomposes by second-order kinetics with an activation of energy of 28,000 cal/mole. In carbon tetrachloride, first, the reaction order is changed—the reaction becomes first order. Second, with equal concentrations  $(1.5 \times 10^{-3} \text{ mole/litre})$  and temperatures (71 and 55°C) the reaction is accelerated by 30-40 times. It is possible that the presence of a solvent in this case plays the same role as the increase of the pressure of the reacting gas itself, keeping the unimolecular constant at the limiting level in accordance with the Lindemann scheme (see Chapter 7, Sec. 7.2). It should however be noted that about 5.5 per cent of ozone participates in a side reaction with CCl<sub>1</sub>, forming chlorine, phosgene, and oxygen. Therefore, the possibility is not excluded that the mechanism will be fundamentally changed.

## 12.2. Application of the Collision Theory to Bimolecular Reactions in Solution

The simple collision theory of bimolecular gaseous reactions [see Chapter 7, Eqs. (7.12) and (7.16)] gives the following expression for the rate constant:

$$k = z_0 e^{-\frac{E}{kT}}$$

where  $z_0$  represents the frequency factor equal to

$$z_0 = \frac{N_{\rm A} D_{\rm AB}^2}{1000} \left\{ 8\pi RT \left( \frac{1}{M_{\rm A}} + \frac{1}{M_{\rm B}} \right)^{1/2} \right\} \text{ litre/mole} \cdot \text{sec}$$

Moelwyn-Hughes used this formula to calculate the values of  $z_0$  for a large number of second-order reactions in solution and compared them with the experimentally found pre-exponential factors of the Arrhenius equation. Table 12.3 lists some data obtained in this way. Among the first reactions are the reactions investigated in the last century by Conrad, and also by Hecht, Conrad and Bruchner. These are the interactions of sodium alkoxides with various alkyl iodides:

$$C_2H_5ONa + RI \longrightarrow C_2H_5OR + NaI$$

The kinetics of reactions of this type were also studied by Arrhenius. As can be seen from Table 12.3, the values of the ratio  $k_{\rm cal}/k_{\rm obs}$  are close to unity for most of the reactions, which supports the applicability of the simple formula of collision theory (7.16) to reactions in liquid solutions. Even reactions that involve ions may also be described by this scheme, though in general, according to the theory of Bronsted, Bredig, and Christiansen, in ionic reactions it is necessary to take into account the "crowding" of ions in "ion atmospheres", and also the effect of the ionic

TABLE 12.3. Comparison of the Calculated and Experimentally Observed Rates of Some Bimolecular Reactions in Liquid Solutions

Reaction	Solvent	A, × 10 <sup>-11</sup> litre/molesec	z₀, × 10 <sup>−11</sup> litre/mole· ·sec	E, keal/mole	kcal kobs
$CH_3ONa + 1,2,4-CIC_6H_3(NO_3)_2$	СН <sub>3</sub> ОН	1.91	2.42	17.45	1.3
$C_2H_5ONa + 1,2,4-CIC_6H_3(NO_3)_2$	C <sub>2</sub> H <sub>5</sub> OH	1.80	2.39	16.76	1.3
$C_2H_5ONa + CH_3I$	$C_2H_5OH$	2.42	1.93	19.49	0.8
$C_2H_5ONa + C_2H_5I$	C <sub>2</sub> H <sub>5</sub> OH	1.49	2.23	20.65	1.5
$C_2H_5ONa + C_6H_5CH_2I$	$C_2H_5OH$	0.15	2.17	19.90	14.5
$C_6H_5ONa + C_3H_7I$	C <sub>2</sub> H <sub>5</sub> OH	3.53	2.31	22.45	0.7
$C_6H_5ONa + iso-C_6H_7I$	C <sub>2</sub> H <sub>5</sub> OH	1.74	2.31	22.10	1.3
$C_6H_5ONa + C_{16}H_{33}I$	C <sub>2</sub> H <sub>5</sub> OH	2.78	2.92	22.43	1.0
$C_6II_5CH_2ONa + C_4II_9I$	$C_2H_5OH$	2.92	2.43	21.56	0.8
$C_6H_5CH_2ONa + iso-C_4H_9I$	$C_2H_5OH$	2.45	2.43	21.35	1.0
$C_6H_5CH_2ONa + C_{16}H_{33}I$	C <sub>2</sub> H <sub>5</sub> OH	1.26	3.12	21.09	2.5
o-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> ONa + CH <sub>3</sub> I	C₂H₅OH	1.30	1.99	21.18	1.5
m-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> ONa + CH <sub>3</sub> I	C₂H₅OH	2.27	1.99	19.49	0.9
$p\text{-}CH_3C_0H_1ON_0 + CH_3I$	CH OH	8.49	1.99	20.9	0.2
$\beta$ -C <sub>10</sub> H <sub>7</sub> ONa + C <sub>2</sub> H <sub>5</sub> I	CH <sub>3</sub> OH C <sub>2</sub> H <sub>5</sub> OH	0.1 0.11	2.21 2.21	21.01 19.84	22.1 20.1
$\beta$ - $C_{10}H_7ONa + C_2H_5I$ $\beta$ - $C_{10}H_7ONa + C_2H_5I$	$C_3H_7OH$	0.11	2.21	21.30	5. <b>5</b>
$CH_3ONa + o-C_6H_4(NO_2)_2$	CH <sub>3</sub> OH	6.11	2.48	20.59	0.4
$C_2H_5ONa + o-C_6H_4(NO_2)_2$	C <sub>2</sub> H <sub>5</sub> OH	3.03	2.45	20.48	0.8
$(CH_3)_2SO_4 + NaCNS$	CH <sub>3</sub> OH	0.19	1.91	17.36	10.0
$CH_2ICOO^- + C_6H_5O^-$	H₂O	0.4	1.85	21.01	4.6
CH <sub>2</sub> ICOOH + CI	$H_2O$	7.9	2.66	22.85	0.3
CH <sub>2</sub> ICOOH + CNS	H <sub>2</sub> O	0.4	2.17	18.19	5.4
$CH_2OHCH_2CI + OH^-$	H <sub>2</sub> O	25.5	2.78	19.87	0.1
$CH_3(CH_2)_3Cl + I^-$	(CH <sub>3</sub> ) <sub>2</sub> CO	1	1.64	23.5	0.7
$C_6H_5CO(CH_2)_2CI+I$	(CH <sub>3</sub> ) <sub>2</sub> CO	f	1.88	22.16	0.2
$CH_3S(CH_2)_2CI + I^-$	(CH <sub>3</sub> ) <sub>2</sub> CO	0.085	1.57	20.74	18.5
$C_2 I I_5 Br + OH^-$	C <sub>2</sub> H <sub>5</sub> OH	4.30	3.86	21.4	0.9
$C_3H_6Br_2+I^-$	CH <sub>3</sub> OH	1.07	1.39	25.10	1.3
CH <sub>2</sub> CICOOH + OH	H <sub>2</sub> O	4.55	2.86	25.85	0.6
.CH <sub>2</sub> .	1120	4.00	2.00	29.00	0.0
$C_6H_4$ $O + OH^-$	$H_2O$	41.7	2.93	12.50	0.07
`co'					

strength. In Table 12.3, the highest value of  $k_{\rm cal}/k_{\rm obs}$  is equal to 20-22 and the lowest is 0.07. In the first case, a steric or probability factor should have been introduced, the inclusion of which could have been associated with the deactivation of the reacting molecules on collisions with the solvent or with the stabilizing action of the solvent by way of formation of some complexes. In the second case, i.e.,  $k_{\rm cal}/k_{\rm obs} = 0.07$ , catalysis may be suspected.

In connection with Table 12.3 the following remark may be made. The theoretical values of  $z_0$  for different reactions differ little from one another. This is accounted for by the fact that the effect caused by the faster motion of light molecules is eliminated by their small diameter; on the other hand, more slowly moving heavy molecules have a larger diameter. As a result, there is obtained the averaged theoretical value of the pre-exponential factor [Eq. (7.17)]:

$$z_0 = 2.8 \times 10^{11}$$
 litre/mole · sec

(see Chapter 7). The applicability of the simple collision theory becomes more spectacular if we take into account the difference in the reaction rates presented in Table 12.3. It is determined by the value of exp  $(\Delta E/RT)$  and amounts to  $10^9$ , i.e., one milliard.

In Chapter 7 we presented the graph (Fig. 7.3) showing the distribution of a large number of reactions in solution (about 200 reactions have been studied) according to the values of A. According to this statistics, about 40 per cent of the reactions have "normal" rates, i.e., their pre-exponential factors are close to the theoretical value  $(2.8 \times 10^{11})$ . Other reactions are "fast", but these reactions are more likely to fall into the category of catalyzed reactions. The third category includes "slow" reactions.

#### 12.3. Slow Reactions in Solution

The contribution made by the Russian scientist N. A. Menshutkin to the development of chemical kinetics is usually underestimated in academic and, perhaps, even in scientific literature. It should however be recalled that, apart from the fundamental works on autocatalysis, Menshutkin discovered (1887) a special class of reactions, a discovery that had a substantial impact in general on the development of chemical kinetics. The reactions in question are those involving the combination of tertiary alkylamines with alkyl halides. For example,

$$(C_2H_5)_3N + C_2H_5I \longrightarrow (C_2H_5)_4NI$$

The specific feature of this type of solution reactions is their very slow rate with a relatively low energy of activation. As seen from Tables 12.4 and 12.5, the activation energies of these reactions lie

TABLE			the Arrhenius autkin Reaction	
	<del></del>	,		<del></del>

Reaction	Solvent	A, litre·mole <sup>-1</sup> · ·sec <sup>-1</sup>	E, kcal/mole	P
$(C_2H_5)_3N + C_2H_5Br$	C <sub>6</sub> H <sub>6</sub> CH <sub>3</sub> COCH <sub>3</sub>	$ \begin{array}{c c} 2.8 \times 10^{2} \\ 8.5 \times 10^{3} \end{array} $	11.2 11.7	$\begin{array}{ c c c c c }\hline 5.3 \times 10^{-10} \\ 1.6 \times 10^{-8} \\ \hline \end{array}$
$C_6H_5(CH_3)_2N + CH_3I$	C <sub>6</sub> H <sub>5</sub> NO <sub>2</sub> C <sub>2</sub> H <sub>2</sub> Cl <sub>4</sub>	$ \begin{array}{c c} 2.6 \times 10^{4} \\ 2.1 \times 10^{4} \end{array} $	13.0 11.7	$ \begin{array}{ c c c c c } \hline 5.3 \times 10^{-8} \\ 4.8 \times 10^{-8} \end{array} $
$C_6H_5(CH_3)_2N + C_2H_5I$	CH₃COCH₃	$2.7 \times 10^4$	13.7	$6.3\times10^{-8}$

TABLE 12.5. The Effect of Solvent on the Rate of the Menshutkin Reaction  $C_2H_5I + (C_2H_5)_3N \rightarrow (C_2H_5)_4NI$  at 100 °C

	$k \times 10^{5}$	A		
Solvent	litre•m	litre·mole-1·sec-1		
Hexane	0.5	ca. $1.0 \times 10^{4}$	16.0	
Cyclohexane	1.0	$1.0 \times 10^{5}$	17.0	
Toluene	25.3	$1.0 \times 10^4$	13.0	
Benzene	39.8	$2.0 \times 10^{3}$	11.4	
Diphenylmethane	64.0	$4.0 \times 10^{3}$	11.8	
Diphenyl ether	117	$8.0 \times 10^{3}$	11.7	
Bromobenzene	160	$4.0 \times 10^4$	12.5	
Iodoben <b>z</b> ene	265	$2.5 \times 10^4$	11.9	
Benzonitrile	1125	$1.0 \times 10^5$	11.9	
Nitroben <b>z</b> en <b>e</b>	1383	$8.3 \times 10^{4}$	11.6	

within the range 11-16 kcal/mole, and their "slowness" manifests itself in the extremely low values of the pre-exponential factor A. Indeed, the pre-exponential factors for these reactions have values of the order of magnitude of  $10^2$  to  $10^4$  instead of the "normal" value  $(2.8 \times 10^{11} \text{ litre·mole}^{-1} \cdot \text{sec}^{-1})$ . This corresponds to steric factors amounting even to  $10^{-10}$ , i.e., one of the ten milliard active collisions proves to be fruitful.

To explain such slow rates, one would think that we should admit the participation of a solvent in the reaction. This idea is suggested, in particular, by the considerable effect of the nature of the solvent on the rate of the Menshutkin reactions.

Table 12.5 lists some relevant data for the reaction between  $(C_2H_5)_3N$  and  $C_2H_5I$ , the constants being arranged in increasing order. As seen, when going from a "neutral" solvent (hexane) to nitrobenzene the rate of the reaction increases rather significantly, by a factor of 2800. When comparing a large body of data we may come to the conclusion that the reaction always proceeds faster in an aromatic than in a corresponding aliphatic solvent. In general, hydrocarbons and ethers are solvents in which reactions proceed slowly, and alcohols and ketones speed up reactions.

What is the role of a solvent? It has been suggested that it is the solvent that slows down the reaction. According to Christiansen, collisions with solvent molecules deactivate the reactant molecules. Other authors believe that the cause of the abnormal slowness of reactions in solution is the formation of relatively stable complexes with solvents—so-called solvates, which retard the reaction of combination of reactant molecules. However, as has been found, the reaction given here as an example proceeds slowly and in the gas phase its rate is only 5 times greater than in hexane and is even lower than in a solution of  $CCl_4$ , which, considering the decomposition of  $N_2O_5$ , is one of the most inert solvents.

The same may be said about another slow reaction, which was also originally studied by Menshutkin:

$$(CH_3CO)_2O + C_2H_5OH \longrightarrow CH_3COOC_2H_5 + CH_3COOH$$

The constants in the Arrhenius equation for this reaction are as follows:  $A = 9.16 \times 10^4 \, \mathrm{litre \cdot mole^{-1} \cdot sec^{-1}}$  and  $E = 12.4 \, \mathrm{kcal/mole}$  in hexane,  $A = 4.14 \times 10^5 \, \mathrm{litre \cdot mole^{-1} \cdot sec^{-1}}$  and  $E = 13.4 \, \mathrm{kcal/mole}$  in CCl<sub>4</sub>. And, what is most interesting, the reaction rate in the gas phase is of the same order of magnitude as in the two inert solvents. Thus, the idea that the reaction is slowed down by solvents may be rejected.

Moelwyn-Hughes maintains that slow reactions in neutral solvents may be regarded as normal reactions in the sense that ao solvent effect is involved. The same solvents in which the slow reaction proceeds relatively rapidly (say, in nitrobenzene) act as catalysts. The catalytic activity of a solvent increases in parallel with the increase of its dielectric constant and of the dipole moment of the molecules.

Another explanation for the slowness of the Menshutkin reactions is that the reaction can be accomplished on collision of activated molecules which are in suitable internal states. For example, when one of the vibrating atoms is near the largest deviation from the normal position. This must reduce the number

of effective collisions by an amount close to the vibration frequency of the given atom and thus bring the experimental data into agreement with collision theory.

#### 12.4. Catalysis in Solution

Perhaps, there will be no exaggeration if we state that most reactions in solution are catalyzed if not only a deliberately introduced catalyst but also the effect of the solvent and the possibility of the formation of a catalyst during the course of the reaction (autocatalysis) are taken into account.

Generally, the term catalysis is used at present for a wide range of phenomena associated with the acceleration of reactions by some substances (or bodies) called catalysts which are either specially introduced into the reacting system or formed in it during the course of the reaction. While taking an active part in the reaction, the catalyst remains chemically unchanged at the end of the reaction.

Numerous observations have led to two important generalizations in the field of catalysis. First, the decrease of the energy of activation as the most pronounced manifestation of the activity of the catalyst. Second, specially for homogeneous \* catalysis in solutions, the concept of the *proportionality* between the reaction rate and the concentration of the catalyst. These propositions lead, of necessity, to the conclusion that a catalyst participates in the reaction, forming certain unstable intermediate compounds or complexes and thus makes it possible for the reaction to proceed along a more energetically favourable pathway.

It is obvious that this point of view is drastically different from the views of Berzelius who introduced the terms catalysis and catalyst: catalysis was regarded by him as the manifestation of the action of some mysterious force vis occulta. Later, Ostwaid tried to describe the rate of the reaction by a formula of the type

of Ohm's law:

 $reaction rate = \frac{driving force of the reaction}{passive resistance}$ 

From this standpoint a catalyst reduces the "passive resistance",

playing the role of a lubricant.

If we return to the modern standpoint, we may state that probably in any case of homogeneous catalysis there are formed labile intermediate products in the early stages. Sometimes these are ordinary chemical compounds which are only of transient existence and which can be isolated and studied separately. Be-

<sup>\*</sup> Discussion of heterogeneous catalysis is beyond the scope of the present book.

cause of the extremely low stability of other intermediate compounds, they cannot be isolated and the formation of such an intermediate may be judged only by the change in some property of the solution: the temporary change of the colouration of the solution, the change of the electrical conductivity, etc.

The oxidation of thiosulphate by hydrogen peroxide to form

tetrathionate is accelerated by iodide ions:

$$2S_2O_3^{2-} + H_2O_2 + 2H^+ \xrightarrow{1^-} S_4O_6^{2-} + 2H_2O$$

There is ground for stating that the intermediate product here is the hypoiodite ion and the reaction proceeds in two stages

(1) 
$$I^- + H_2O_2 \longrightarrow IO^- + H_2O$$

(2) 
$$2S_2O_3^{2-} + IO^- + 2H^+ \longrightarrow S_4O_6^{2-} + H_2O + I^-$$

the sum of which evidently gives the overall equation.

The oxidation of thiosulphate by hydrogen peroxide in the presence of another catalyst, molybdic acid, proceeds with the formation of sulphate:

$$S_2O_3^{2^-} + 4H_2O_2 \xrightarrow{MoO_4^{2^+}} 2SO_4^{2^-} + 2H^+ + 3H_2O$$

In this case, the intermediate formation of the permolybdate ion is very probable:

$$4\text{MoO}_4^{2-} + 4\text{H}_2\text{O}_2 \longrightarrow 4\text{MoO}_5^{2-} + 4\text{H}_2\text{O}$$
  
 $\text{S}_2\text{O}_3^{2-} + 4\text{MoO}_5^{2-} + \text{H}_2\text{O} \longrightarrow 2\text{SO}_4^{2-} + 4\text{MoO}_4^{2-} + 2\text{H}^+$ 

With account taken of transition-state theory, the following scheme may be suggested for catalysis in solution. Let us say, the reaction between the substances A and B in the absence of a catalyst proceeds with the formation of an activated complex  $AB^{\neq}$ ;

$$A + B \longrightarrow AB \neq \longrightarrow C + D$$

In the presence of a catalyst K the process takes place in several stages:

$$(1, 2) A + K \stackrel{k_1}{\rightleftharpoons} AK$$

This is the reversible formation of an intermediate product. The third stage is the formation of an activated complex:

$$(3) AK + B \xrightarrow{k_3} ABK \neq$$

And, finally, the activated complex is decomposed into the products and the catalyst:

(4) 
$$ABK \stackrel{\neq}{\longrightarrow} C + D + K$$

Employing the method described in Chapter 8, it is basically

possible to construct a potential-energy surface and to imagine the energy profiles for the paths of the uncatalyzed and catalyzed reactions. An approximate theoretical picture is presented in Fig. 12.1.

As seen, the exothermic formation of an intermediate is expected in this case on catalysis, after which the potential energy of the reacting system increases because of the formation of the

activated complex  $ABK^{\neq}$ . From Fig. 12.1 it is seen that the energy of activation decreases, i.e., this energy being required for the formation of the activated complex from the reactants. It is equal to the difference between the zero-point levels of  $AB^{\neq}$  and  $ABK^{\neq}$ , i.e.,  $\Delta E$ . If the auxiliary effect of the catalyst on the pre-exponential factor is neglected, the ratio of the rate constants of the catalyzed and uncatalyzed reactions may be represented in the form

$$\frac{k_{\text{cat}}}{k_{\text{uncat}}} = e^{\frac{\Delta E}{RT}}$$
 (12.1)

Since  $\Delta E$  is contained in the exponent, then even a slight decrease of the energy of activa-

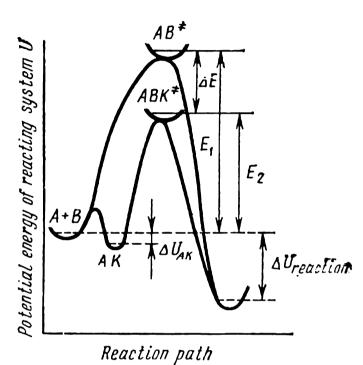


Fig. 12.1. The energy profiles of uncatalyzed and catalyzed reactions:  $E_1$ —activation energy of an uncatalyzed reaction;  $E_2$ —activation energy of a catalyzed reaction.

tion may result in a rather considerable acceleration of the reaction. As an example, let us consider the decomposition of acetaldehyde, which proceeds in the gas phase at 800 K:

$$CH_3CHO \xrightarrow{I_2} CH_4 + CO$$

The reaction is accelerated by iodine vapour,  $E_1$  being equal to 45,500 and  $E_2$  to 32,500 cal/mole. Thus,  $\Delta E = 13,000$  cal/mole and is about 28 per cent. But, using formula (12.1), we obtain

$$\frac{k_{\text{cat}}}{k_{\text{uncat}}} = e^{\frac{13,000}{2800}} \approx 10^{3.5} \approx 3000$$

that is, in the presence of a catalyst the reaction proceeds by 3000 times faster.

The kinetics of a homogeneous catalyzed reaction written in the form of a sequence of three processes (1 and 2, 3, 4) depend on the properties of the intermediate AK. To consider this problem, let us first write the observed reaction rate, which is equal to the rate of the unimolecular decomposition of the activated complex:

$$\omega = \frac{d [C]}{dt} = k_4 [ABK^{\neq}]$$
 (12.2)

In the stationary state the concentration of the activated complex can be determined from the relation

$$k_3 [AK][B] = k_4 [ABK \neq]$$
 (12.3)

Applying the steady-state principle to the intermediate AK, we get

$$k_1[A][K] - k_2[AK] - k_3[AK][B] = 0$$
 (12.4)

Determining the concentration [ABK $\neq$ ] from Eqs. (12.3) and (12.4) and substituting it into Eq. (12.2), we obtain an expression for the observed reaction rate:

$$w = \frac{d[C]}{dt} = \frac{k_1 k_3 [A] [B]}{k_2 + k_3 [B]} [K]$$
 (12.5)

This equation lies at the basis of the kinetics of homogeneous catalytic reactions. First, in accordance with experiment, it establishes the proportionality between the reaction velocity and the concentration of the catalyst. Second, two extreme cases can be distinguished in the analysis of the reaction scheme. Thus, for example, the rate constant for the reverse decomposition of the intermediate AK may be found to be much greater than the rate constant for its further conversion, i.e.,

$$k_2 \gg k_3$$
 and  $k_2 \gg k_3$  [B] (12.6)

In other words, the intermediate is largely decomposed into the reactants and is converted but at a low rate into the activated complex and further into the end products. In this case the concentration of the intermediate will be close to the equilibrium value, and the quantity  $k_3$  [B] in the denominator of Eq. (12.5) may be neglected as compared with  $k_2$ , i.e.,

$$w = \frac{d[C]}{dt} = \frac{k_1 k_3}{k_2} [K] [A] [B] = k_{II} [A] [B]$$
 (12.7)

In other words, the reaction in this case must be second order with respect to the reactants with the rate constant being proportional to the concentration of the catalyst:

$$k_{11} = \frac{k_1 k_3}{k_2} \left[ K \right]$$

Perhaps, it would be better to speak in this case of the ordinary reaction order with respect to both reactants. Intermediates having such properties, i.e., those essentially present in the reacting

system in an equilibrium concentration, are called the **Arrhenius** complexes. The origin of this term is connected with the fact that the activated form of the molecule, the existence of which was assumed in the derivation of the temperature dependence of the reaction rate (see Chapter 4), belongs to entities of this type.

In the other of the two extreme cases it may be found that

$$k_2 \ll k_3$$
 and  $k_2 \ll k_3$  [B]

that is, as the intermediate is formed it will immediately react further to give the end products. Now, the quantity  $k_2$  in the denominator of Eq. (12.5) may be neglected as compared with  $k_3$  [B] and the reaction rate

$$w = k_1 [K] [A]$$

will not in general depend on the concentration of the second reactant since at any, even small concentrations its amount will be sufficient for the immediate consumption of AK. An intermediate complex of this type is frequently called a **van't Hoff complex** because since the time of van't Hoff such complexes are used to account for the decrease of the observed overall reaction order as compared with the plausible assumptions. It may be said that in this particular case the reaction is zero order with respect to the substance B. The concentration of the van't Hoff complex must evidently be far from the equilibrium value in contrast to the Arrhenius complex.

#### 12.5. Acid-Base Catalysis

A large number of reactions in solution are speeded up in the presence of acids and bases. To this category of reactions belongs the well-known hydrolytic cleavage of an ester:

$$RCOOC_2H_5 + H_2O \longrightarrow RCOOH + C_2H_5OH$$

We may also cite the inversion of polysaccharides, say, of sucrose disaccharide:

$$C_{12}H_{22}O_{11} + H_2O \longrightarrow 2C_6H_{12}O_6$$

Mention should also be made of some reactions of isomerization; for example, the mutarotation of glucose which has already been mentioned in the text (see Chapter 3). Among such reactions is also the mutarotation of beryllium camphorbenzoate or nitrocamphor. The latter mutarotation is associated with an isomerization of this type:

$$C_8H_{14}$$
 $CO$ 
 $CO$ 
 $CNO_2H$ 
 $CO$ 

It is precisely in connection with the investigations of isomerization reactions accompanied by mutarotation that Lowry advanced the concept which may be called the donor-acceptor theory of acid-base catalysis. This theory is based on two observations. First, it has been found that the mutarotation of various compounds, which proceeds readily in water, fails to take place in the various pure non-aqueous solvents. For example, tetramethylglucose undergoes no change either in dry cresol (an acid) or in dry pyridine (a base). Placed in specially cleaned quartz vessels tetraacetylglucose and tetramethylglucose remain unchanged for a long time in solvents such as chloroform, benzene, and methyl acetate.

However, second, while pure cresol and pure pyridine do not separately accelerate the mutarotation, in the presence of a mixture of 1 part of m-cresol and 2 parts of pyridine the reaction of conversion of  $\alpha$ -glucose into  $\beta$ -glucose proceeds by about 20 times faster than in water. It has also been established that a mixture of pyridine and water is a better catalyst than water alone, and mixtures of methanol and pyridine or m-cresol are more active than the pure alcohol. According to Lowry (1925-1928), acid-base catalysis consists of the transfer of a proton from the donor-acid part of the catalyst to the substrate molecule and the expulsion of a proton (probably, another proton) by the acceptor (base) part of the catalyst. First, water itself is such a proton donor-acceptor. Dissociating into ions

$$H_2O \longrightarrow OH^- + H^+$$

water is a proton donor and when it binds a proton

$$H^+ + H_2O \longrightarrow H_3O^+$$

it exhibits proton-acceptor properties. These properties of water can be amplified by addition of acids or bases, as a result of which many reactions are accelerated. For instance, according to the data obtained by Hudson (1907) the effect of hydrogen and hydroxyl ions on the mutarotation of glucose is determined by the equation

$$k = 0.0096 + 0.258 [H3O+] + 9750 [OH-]$$
 (12.8)

where k is the rate constant for the mutarotation. The supposed mechanism of acid-base catalysis can be traced out on the thoroughly studied iodination of acetone:

$$CH_3COCH_3 + I_2 \longrightarrow CH_3COCH_2I + I^- + H^+$$

The empirical rate equation for this reaction may be represented in the following form:

$$-\frac{d \text{ [acetone]}}{dt} = k \text{ [acetone]} [H^+]$$
 (12.9)

that is, the reaction rate is proportional to the concentration of hydrogen ions and acetone and does not depend (zero order) on the concentration of iodine. The enol form of the ketone is first formed by the donor-acceptor mechanism:

$$CH_3$$
— $C$ — $CH_3$  +  $H^+$  —  $CH_3$ — $C^+$ — $CH_3$  Proto-
nation

The resulting enol form reacts then readily with iodine:

$$CH_3-C=CH_2+I_2 \longrightarrow CH_3-C-CH_2I+H^++I^-$$
OH
O

The slower rate-determining step is the first step, which is represented by Eq. (12.9) and the intermediate complex, i.e.,  $CH_3COH = CH_2$ , should be qualified as belonging to the category of van't Hoff complexes.

## 12.6. Intermediates in Homogeneous Catalysis. The Shpitalsky Mechanism

The development of the hypothesis of the mechanism of homogeneous catalysis, in which it is assumed that intermediates are formed by the interaction between the catalyst and the reacting substance (the substrate), is tied up with the names of many scientists: Bredig, Braude, Abel, and also Henri and Michaelis. All the authors listed are the predecessors of Shpitalsky, in whose works the "classical" theory of intermediate compound formation was most thoroughly elaborated.

The Shpitalsky theory was based on the following propositions which had been suggested earlier (1-5) and those which have been reformulated anew (6-10):

- 1. A catalyst is a substance that renders the substrate reactive by forming a labile intermediate complex with it, i.e., with the substrate.
- 2. The formation of an intermediate complex is a relatively fast reversible process.
- 3. The labile intermediate complex undergoes a further, irreversible relatively slow change.

- 4. The overall rate of the catalyzed reaction is proportional to the concentration of the intermediate complex and not to the substrate concentration.
- 5. Depending on the value of the equilibrium constant for the formation of an intermediate complex the fraction of the combined catalyst in it remains to be in a free state.
- 6. The formation of intermediate complexes may simultaneously involve many substances, so that a number of catalysts will function, by way of the formation of a single intermediate complex, as a *single mixed catalyst*.

7. Apart from the catalyst, some "associated substances" \*, mainly the ions H<sup>+</sup> and OH<sup>-</sup>, may be involved in the formation of intermediate complexes.

- 8. Apart from participating in the formation of intermediate complexes, "associated substances" may exert an influence on the lability of the intermediate compound and, hence, on the rate of its decomposition, even without taking part in the process of its reversible formation.
- 9. One and the same catalyst may simultaneously form many intermediates with the substrate.
- 10. When the simultaneous action of many catalysts is involved (6) or when many intermediates are formed from one catalyst (9), the resultant reaction rate is the sum of the rates of decomposition of the individual intermediates.

Proceeding from the possibilities listed above, Shpitalsky derives more or less complicated kinetic equations, including the simplest Henri-Michaelis equation.

Here we shall consider in more detail only two versions which have been confirmed experimentally in an elegant manner. Namely, we shall be concerned, first, with the formation of two intermediates,  $M_1$  and  $M_2$ , by one catalyst and one substrate according to the following stoichiometric equations:

$$F + S \rightleftharpoons M_1$$

$$F + 2S \rightleftharpoons M_2$$

Thus, the catalyst molecule F forms reversibly intermediate complexes with one and two substrate molecules.

Assuming the formation of equilibrium concentrations of the intermediate complexes in accordance with propositions 2 and 3, we write the equilibrium constants:

$$\frac{c_{M_1}}{c_{S}\left(c_{F}-c_{M_1}-c_{M_2}\right)}=K_1 \tag{12.10}$$

<sup>\*</sup> My quotation marks (E. Yeremin).

and

$$\frac{c_{M_2}}{c_S^2 \left(c_F - c_{M_1} - c_{M_2}\right)} = K_2 \tag{12.11}$$

According to propositions 4 and 10, the overall rate of the reaction will be represented thus:

$$w = -\frac{dc}{dt} = k_1 c_{M_1} + k_2 c_{M_2} \tag{12.12}$$

Or, on combined solution of Eqs. (12.10), (12.11), and (12.12),

$$w = -\frac{dc}{dt} = \frac{c_{\rm F} \left( k_1 K_1 c_{\rm S} + k_2 K_2 c_{\rm S}^2 \right)}{1 + k_1 c_{\rm S} + k_2 c_{\rm S}^2}$$
(12.13)

According to this equation, the reaction rate is always proportional to the concentration of the catalyst. As to the rest, however, the kinetics may be extremely varied. Thus, for example, if the values of  $K_1$ ,  $K_2$ , and  $k_1$  are small as compared with  $k_2$  and with unity, the reaction rate is expressed by a simple second-order equation:

$$w = -\frac{dc}{dt} = c_{\rm F} k_2 K_2 c_{\rm S}^2 \tag{12.14}$$

But if  $k_2$  is very small,  $K_2$  is large and simultaneously  $K_1$  is small and  $k_1$  is very large, the following equation may be obtained:

$$w = -\frac{dc}{dt} = \frac{k_1 K_1}{K_2} \cdot \frac{c_F}{c_S} \tag{12.15}$$

which expresses the reaction rate which is inversely proportional to the substrate concentration. Evidently, in the first of the cases examined the reaction is "carried" by the second intermediate  $M_2$  owing to its being labile. The first intermediate, though being formed, is decomposed very slowly. In the second case, the second intermediate  $M_2$  is predominantly formed—its equilibrium constant is great, but the catalytic reaction is "carried" by the first intermediate  $M_1$  which is considerably labile but is present in small concentrations which are constantly being recovered.

If we specify the arbitrary values of the constants, we can plot, in accordance with Eq. (12.13), theoretical dependences of the reaction rate on the concentration of the substrate.\* Figure 12.2

<sup>\*</sup> The calculations were carried out by E. I. Shpitalsky in collaboration with N. I. Kobozev.

shows various types of kinetic curves obtained by using the arbitrary values of the constants  $K_1$ ,  $k_1$ ,  $K_2$ , and  $k_2$  listed below:

	1	2	<b>3</b>	4	5	6	7
$K_1$	$10^{-7}$	$10^{3}$	5×10¹	8	8	5×10	1.0
$k_1$	$10^{-4}$	10-7	10-4	$10^{-3}$	$10^{-3}$	10-3	1.0
		$4 \times 10^{-3}$	102	$10^5$	10	$10^2$	105
		102	$10^{-3}$	10-4	10-1	$10^{-3}$	0

As can be seen from Fig. 12.2, even in reactions, which are quite analogous to one another from the standpoint of stoichio-

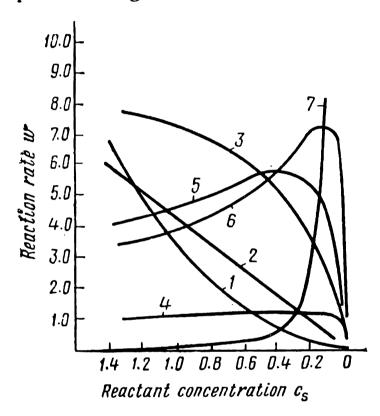


Fig. 12.2. The rate of a catalyzed reaction versus the concentration of the reagent for the simultaneous formation of two intermediates:

1—second order; 2—first order; 3—fractional order (smaller than unity); 4—zero order; 5, 6, 7—curves of the autocatalytic type—a reaction with acceleration.

metry, and in the process of formation of two intermediates according to the reaction equations given page 346, the kinetics may be quite different, depending on the relative values of the constants  $K_1$ ,  $k_1$ ,  $K_2$ , and  $k_2$ . Namely, there may be observed a second-order reaction (1) and, equally well, first-order reaction (2). These may be followed by a fractional order (3)zero order (4). Finally, the reaction may be accelerated, i.e., it may be described by curves of the autocatalytic type.

Passing over to the second version, we note that when three intermediates are involved, the rate curve may pass first through a minimum with disappearance of the reactant and then through

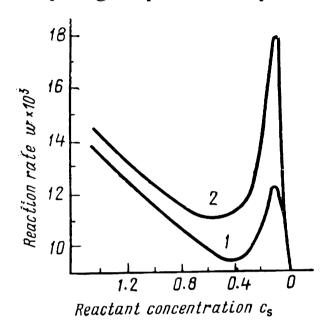
a maximum. In this case, the overall rate equation may be written in the form

$$\mathbf{w} = -\frac{dc}{dt} = \frac{c_{\rm F} \left( k_1 K_1 c_{\rm S} + k_2 K_2 c_{\rm S}^2 + k_3 K_3 c_{\rm S}^3 \right)}{1 + K_1 c_{\rm S} + K_2 c_{\rm S}^2 + K_3 c_{\rm S}^3}$$
(12.16)

To this equation there may correspond the kinetic curves shown in Fig. 12.3. As can be seen, apart from the minimum, these curves calculated from the adopted values of the constants pass through a sharply prominent maximum. The shape of the curves and the

position of the extrema are highly sensitive to the change of the constants  $K_1$ ; for the two curves in Fig. 12.3, five of the six constants are exactly identical and only the equilibrium constant  $K_1$  is greater by a factor of 1.5 in the second case than in the first.

The Shpitalsky theory has been successfully applied by Shpitalsky himself and also by Kobozev to the catalytic decomposition of hydrogen peroxide by chromic acid (chromates) in the first



80 70 × 2 × 30 × 30 10 8 6 4 2 0 CH202 × 10<sup>2</sup>, moles/litre

Fig. 12.3. The possible theoretical dependences of the rates of catalyzed reactions on the reactant concentration for the simultaneous formation of three intermediates [Eq. (12.16)]:  $1-K_1=4$ ;  $2-K_1=6.0$ . The remaining constants are equal for the two curves:  $k_1=10^{-1}$ ;  $K_2=2\times10^2$ ;  $k_2=10^{-3}$ ;  $K_3=10^2$ ;  $k_3=3\times10^{-2}$ .

Fig. 12.4. The kinetics of the decomposition of hydrogen peroxide by  $Cr_2O_7^2$  ions in neutral and acid solutions at  $0^{\circ}C$ :

$$1-c_{\mathrm{HNO_3}} = 0.2;$$
  $2-c_{\mathrm{HNO_3}} = 0.001;$   $3-c_{\mathrm{HNO_3}} = 0.0025;$   $4-c_{\mathrm{HNO_3}} = 0.005$  mole.

place and also by molybdates and tungstates. It has been found that the decomposition of hydrogen peroxide by a neutral dichromate is described by a simple equation, the order of which is dependent on temperature (Fig. 12.4, 1). Namely, at 25 °C the process rather exactly obeys first-order kinetics; at 0 °C the order is less than the first, and at 50 °C it approaches second order. It is presumed that in this case the catalysis is effected by one intermediate which is formed from the ion  $\text{Cr}_2\text{O}_7^{2-}$  and two molecules of hydrogen peroxide. Thus,

$$Cr_2O_7^{2-} + 2H_2O_2 \implies Cr_2O_9^{2-} + 2H_2O$$

The rate of the catalyzed reaction is expressed in this case by the equation

$$w = k \left( c_{\text{Cr}_2 \text{O}_7^2} \right) \frac{K c_{\text{H}_2 \text{O}_2}}{1 + c_{\text{H}_2 \text{O}_2}^2}$$
 (12.17)

Here K is the equilibrium constant for the formation of the intermediate  $\operatorname{Cr}_2\operatorname{O}_9^{2^-}$  and k is the rate constant for its irreversible decomposition. If this scheme is correct, Eq. (12.17) must give a straight line in the coordinates 1/w and  $1/c_{\operatorname{H}_2\operatorname{O}_2}^2$  because

$$\frac{1}{\mathbf{w}} = \frac{1}{kKc_{Cr_2O_2}} \cdot \frac{1}{c_{H_2O_2}^2} + \frac{1}{kc_{Cr_2O_2}}$$
(12.18)

A check-up shows that really in the temperature range studied (0 to 56 °C) there are obtained straight lines. From the data obtained it may be concluded that the catalytic decomposition of hydrogen peroxide is an intramolecular recombination of oxygen atoms which are transferred from the peroxide molecules to the catalyst.

The overall scheme of the catalysis may be depicted thus:

I. Transfer of active oxygen molecules to the catalyst

$$F + 2H_2O_2 \rightleftharpoons F \cdot + 2H_2O$$

II. Recombination of oxygen atoms in the intermediate

$$F \stackrel{O}{\cdot} \rightarrow F + O_2$$

In acid solution, or when chromic acid is used as catalyst, the kinetics of the reaction are found to be very complicated: in the region of considerable concentrations of the peroxide the rate of the reaction passes through a minimum, then through a maximum and, finally, falls sharply to zero. An example of the experimentally obtained curves is presented in Fig. 12.4. For acid solutions the experimental curves are seen to be very similar to the theoretical curves calculated from Eq. (12.20) on the assumption of the formation of three intermediate complexes.

Analysis of the kinetic curves and study of the dependence of their shape on temperature and the acidity of solution lead to the conclusion that when the decomposition of hydrogen peroxide is catalyzed by the ion  $Cr_2O_7^{2-}$  in acid solutions the above-mentioned "neutral" complex  $Cr_2O_9^{2-}$  with a relatively low activity is formed. Second, a very active "acid" intermediate is formed, which causes the appearance of a sharp maximum of the rate at the end of the reaction. This complex is identified with the ion  $HCr_2O_9^{2-}$ , i. e., is the product of the addition of the H+ ion to  $Cr_2O_9^{2-}$ ; it is by several times more active than the neutral complex. Finally, we have to assume the formation of another less active acid complex, the composition of which has not been elucidated, and its participation in catalysis.

In studying the decomposition of hydrogen peroxide by sodium molybdate there were isolated the permolybdates Na<sub>2</sub>MoO<sub>8</sub> and

 $Na_2MoO_6$ , the first of which was identified as the active intermediate that controls the catalytic decomposition. Analogously, for the decomposition of  $H_2O_2$  in the presence of the  $WO_4^{2-}$  ion, it is assumed that the active intermediate is the  $WO_8^{2-}$  ion.

## 12.7. Application of the Theory of the Intermediate Complex Formation to Enzymatic Reactions

Catalytic reactions in solution (mostly in colloidal solutions) play an enormous part in biology. The biological catalysts called **enzymes** are known to be highly efficient, their activity exceeding by many orders of magnitude the activity of artificial catalysts. Another remarkable feature of enzymes is their sharply pronounced specificity. Each of the enzymes effects only one reaction. For example, the enzyme **catalase** accomplishes only one reaction in organisms, namely, it decomposes the hydrogen peroxide formed in some processes as a side product and it does this with a virtually enormous rate. Thus, if the activity of platinum sol, which is one of the most powerful artificial catalysts for the decomposition of hydrogen peroxide may be characterized by the number \*  $7.08 \times 10^2$ , the corresponding number for catalase is equal to  $3.2 \times 10^5$ , i.e., is by three orders of magnitude greater than that of platinum sol.

The mechanisms of enzymatic (enzyme-catalyzed) reactions are extremely complicated and have been studied little. The kinetics of such reactions, however, are often described by simple equations which are derived on the basis of very simple assumptions. For instance, the kinetics of the inversion of cane sugar (sucrose) by the action of the enzyme sucrase (also called saccharase or invertase) is described on the basis of the assumption of the formation of the only intermediate which has the properties of an Arrhenius complex. The further considerations and derivation were proposed by Henri in 1902 and also by Michaelis and Menten in 1913.

Let us denote the enzyme by the letter F and the substrate by S; the kinetic scheme of the reaction may be written thus:

(1) 
$$F + S \Longrightarrow FS$$
  
(2)  $FS \longrightarrow products$ 

At the first stage there is formed an intermediate, the rates of its formation and decomposition being so great that the equilibrium concentration  $c_{\rm FS}$  is set up (i.e., it is almost unaffected by the relatively slow decomposition of FS into the products in the second process). If the relatively small initial concentration of the

<sup>\*</sup> These numbers are first-order rate constants (sec-1) calculated per one active centre (after Kobozev).

enzyme is  $c_F$ , then its equilibrium concentration will be given by  $c_F - c_{FS}$  and the equilibrium constant \* will be

$$K_{\rm c} = \frac{c_{\rm S} \left(c_{\rm F} - c_{\rm FS}\right)}{c_{\rm FS}}$$
 (12.19)

From this we determine the concentration of the intermediate complex:

$$c_{\rm FS} = \frac{c_{\rm S}c_{\rm F}}{K_{\rm c} + c_{\rm S}} \tag{12.20}$$

If we assume that the decomposition of the intermediate complex proceeds by first-order kinetics, the observed rate will be expressed as follows

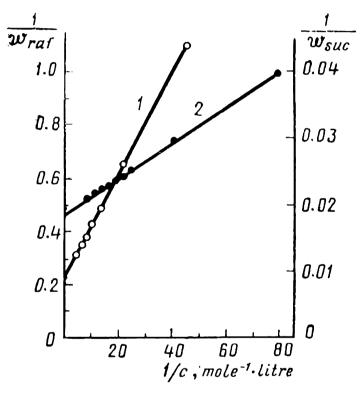


Fig. 12.5. Testing of the Michaelis equation (12.22) for the inversion of sugars in the presence of sucrase; the rates are expressed in arbitrary units:

1-raffinose; 2-sucrose (according to the data obtained by Kuhn, cited by Kobozev).

$$w = \frac{dx}{dt} = kc_{FS} = k \frac{c_{S}c_{F}}{K_{c} + c_{S}} =$$

$$= kc_{F} \frac{k_{1}c_{S}}{1 + k_{1}c_{S}} \quad (12.21)$$

For a given constant concentration of the enzyme the equation may be represented in the form

$$w = k' \frac{k_1 c_S}{1 + k_1 c_S} \quad (12.22)$$

An equation of the type (12.21) or (12.22) is called the **Michaelis equation** in the kinetics of enzyme-catalyzed reactions. It was first applied to the inversion of sucrose by the enzyme saccharase extracted from the yeast; it was subsequently

found that the hydrolysis of esters catalyzed by esterases and also some other enzyme-catalyzed reactions obey the Michaelis equation.

If on the basis of Eq. (12.22) we write the inverse of the rate

$$\frac{1}{w} = \frac{1}{k'} + \frac{1}{k'k_1c_S} \tag{12.23}$$

<sup>\*</sup> Here, by tradition and in contrast to the former, more widespread method of writing the equilibrium constant, the reactant concentrations are written in the numerator.

then, as seen, the applicability of Eq. (12.22) must be confirmed by the straight-line course of the function  $1/w = f(1/c_s)$ . Figure 12.5 gives two examples: the inversion of sucrose and the inversion of raffinose trisaccharide. As can be seen, in these cases Eq. (12.22) is in good agreement with the experimental data.

Attention should be focused on the functional similarity between the Michaelis equation and the equation for the rate of a

heterogeneous gas-phase reaction oblained with the aid of the Langmuir adsorption isotherm for a partially covered surface:

$$\frac{dx}{dt} = \frac{kc}{1+bc} \tag{12.24}$$

This analogy is hardly accidental, the more so that in both cases zero and first orders may be observed in the dependence on the values of the constants and concentrations. Evidently here we have a similarity between the "external" mechanisms, which reveals itself in that in both cases there is formed at equilibrium a transition state and either the surface or "capacity" of the enzyme is completely "filled". It is also essential that an equation of the Michaelis equation type is well justified in the decomposition of hydrogen peroxide catalyzed by platinum black. But not all enzyme-catalyzed reactions obey this equation. For instance, for the earlier mentioned decomposition of hydrogen peroxide in the presence of catalase no linear de-

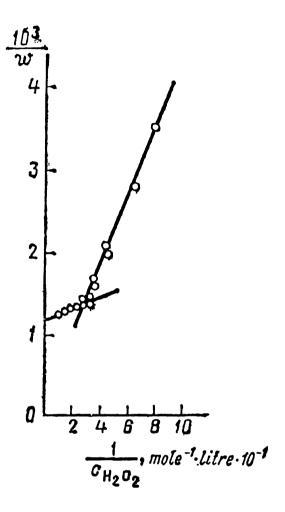


Fig. 12.6. The inapplicability of the Michaelis equation (12.22) to the decomposition of hydrogen peroxide in the presence of catalase.

pendence of 1/w on  $f(1/c_s)$  is obtained. As seen from Fig. 12.6, two straight lines at least are needed here—one for small and the other for high concentrations in order to describe this graph by linear functions.

Kobozev maintains, in conformity with the theory of intermediate complex formation developed by him in collaboration with Shpitalsky, that in this case the catalytic decomposition of hydrogen peroxide is associated with the formation of two intermediates of the Arrhenius complex type and is described by three equa-

tions:

(1a) 
$$F + H_2O_2 \xrightarrow{K_1} FO + H_2O$$
  
(1b)  $F + 2H_2O_2 \xrightarrow{K_2} F \cdot + 2H_2O$   
(2)  $F \cdot \xrightarrow{K_r} F + O_2$ 

Here  $K_1$  and  $K_2$  are the equilibrium constants for the complexes O  $M_1 = FO$  and  $M_2 = F \cdot$ , and  $k_r$  is the rate constant for the uni-

molecular decomposition of the complex F . According to the

theory of intermediate complex formation as formulated by Shpitalsky, we have:

$$K_1 = \frac{c_{M_1}}{\left(c_F - c_{M_1} - c_{M_2}\right) c_{H_1 O_2}} \tag{12.25}$$

$$K_2 = \frac{c_{M_2}}{\left(c_F - c_{M_1} - c_{M_2}\right) c_{H_2 O_2}^2} \tag{12.26}$$

Here, as before, it is assumed that the formation of intermediates in small equilibrium concentrations does not alter the concentration of hydrogen peroxide.

The rate of the reaction is written as follows:

$$w = -\frac{dc_{\text{II}_2\text{O}_2}}{dt} = k_r c_{\text{M}_2} \tag{12.27}$$

Solving these equations, we find directly:

$$c_{\mathbf{M}_{1}} = \frac{K_{1}c_{\mathbf{F}}c_{11_{2}\mathbf{O}_{2}}}{1 + K_{1}c_{11_{2}\mathbf{O}_{1}} + K_{2}c_{\mathbf{H}_{2}\mathbf{O}_{2}}^{2}}$$
(12.28)

$$c_{M_2} = \frac{K_2 c_F c_{H_2 O_2}^2}{1 + K_1 c_{H_2 O_1} + K_2 c_{H_2 O_2}^2}$$
(12.29)

Now on the basis of relations (12.27) and (12.28) we may write an equation for the reaction rate in the form:

$$w = k_r c_F \frac{K_2 c_{H_2 O_2}^2}{1 + K_1 c_{H_2 O_2} + K_2 c_{H_2 O_2}^2}$$
(12.30)

Introducing the notation

$$k_r c_{\downarrow i} = r \tag{12.31}$$

we shall be convinced that Eq. (12.30) can describe the various special cases. Indeed, it yields:

(a) zero order when 
$$K_2 c_{\rm H_2O_2}^2 \gg K_1 c_{\rm H_2O_2} > 1$$
 and  $w = r$ 

since the first two terms in the denominator may be neglected as compared with the third term;

(b) first order when  $K_1 c_{\text{H}_2\text{O}_2} \gg K_2 c_{\text{H}_2\text{O}_2}^2 > 1$  and

$$w = r \frac{K_2}{K_1} c_{\text{H_2O}},$$

(c) second order when  $K_2c_{\rm H_2O_2}^2<1>K_1c_{\rm H_2O_2}$  and  $w=rK_2c_{\rm H_2O_2}^2$ 

(d) an equation of the Michaelis equation type, i.e., a fractional order, higher than zero order and smaller than first order, when  $K_1c_{\rm H_2O_2}\gg 1\ll K_2c_{\rm H_2O_2}^2$  and

$$w = r \frac{\frac{K_2}{K_1} c_{\text{H}_2\text{O}_2}}{1 + \frac{K_2}{K_1} c_{\text{H}_2\text{O}_1}}$$
(12.32)

(e) a fractional order when  $1 \approx K_1 c_{\text{H}_2\text{O}_2} \approx K_2 c_{\text{H}_2\text{O}_2}^2$  and Eq. (12.30) must be used in its complete form. As seen, Eq. (12.30) is capable of providing a highly varied kinetic picture. To compare with experimental data, let us represent Eq. (12.30) in the following form:

$$\frac{c_{\text{H}_2\text{O}_2}}{w} = \frac{1}{rK} \cdot \frac{1}{c_{\text{H}_2\text{O}_2}} + \frac{1}{r} \cdot \frac{K_1}{K_2} + \frac{1}{r} c_{\text{H}_2\text{O}_2}$$
(12.33)

Figure 12.7 shows a theoretical curve plotted in accordance with this equation in the coordinates  $c_{11_2O_2}/w$  and  $c_{11_2O_2}$ . As can be seen, this curve passes through a minimum in the region of small concentrations of hydrogen per-

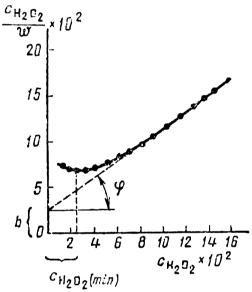


Fig. 12.7. The type of the theoretical curve corresponding to Eq. (12.30) of the theory of the intermediate complex formation for the enzyme-catalyzed decomposition of hydrogen peroxide (the concentration in mole  $\times$   $\times$  litre<sup>-1</sup>; the rate in mole  $\times$   $\times$  litre<sup>-1</sup>·min<sup>-1</sup>) (after N. I. Kobozev).

oxide. At high concentrations the function is linear, the slope being given by

$$\tan \varphi = \frac{1}{r} \tag{12.34}$$

and the intercept on the ordinate

$$b = \frac{1}{r} \cdot \frac{K_1}{K_2} \tag{12.35}$$

At the same time the concentration of the peroxide, which corresponds to the minimum, is connected with  $K_2$ , i.e.,

$$c_{\text{H}_2\text{O}_2\,\text{(min)}} = \frac{1}{\sqrt{K_2}}$$
 (12.36)

Thus, having an experimental curve of the type shown in Fig. 12.7 at our disposal, we can readily find all the constants of Eq. (12.30) that characterize the catalytic process under given conditions. It

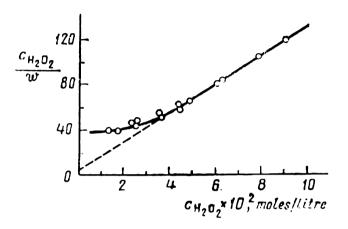


Fig. 12.8. The decomposition of hydrogen peroxide in the presence of catalase. The reaction rate in mole·litre<sup>-1</sup>·min<sup>-1</sup>.

should be noted that the Michaelis equation

$$\frac{c_{\text{H}_2\text{O}_2}}{w} = \frac{1}{rk} + \frac{1}{r} c_{\text{H}_2\text{O}_2} \quad (12.37)$$

would have given a straight line over the entire range of concentrations.

The theoretical curve obtained by Kobozev has been compared with the data on the decomposition of hydrogen peroxide catalyzed by various catalysts—catalase, hemin in

solution, heterogeneous catalysts, platinum black, platinum and gold sols. As an example, Fig. 12.8 presents data for catalase.\* At small concentrations of the peroxide there is a distinct deviation from the linear plot, but the minimum here is not explicitly pronounced. Nonetheless, it is possible to obtain theoretical curves close to the experimental plot by increasing the relative value of the equilibrium constant  $K_2$  for the formation of the intermediate  $F_0^{\circ}$ . Thus, the scheme for the catalysis of the decomposition of hydrogen peroxide by catalase, which involves the reversible formation of two intermediates, is in better agreement with the experimental data than the Michaelis scheme.

#### 12.8. Kinetics of Autocatalytic Reactions

In the category of homogeneous autocatalytic reactions we include reactions that are accelerated due to the formation of a catalyst—the reaction product—during the course of the process. The initial acceleration of the formation of acetanilide in the decomposition of tertiary amylacetate was detected by Menshutkin. The graphical representation of the course of the reaction in the

<sup>\*</sup> H. von Euler and K. Josephson, Lieb. Ann. and Chem., 455, 1 (1927); 456, 11 (1927).

coordinates "the amount of ester decomposed" and "the time" gave a typical sigmoid curve with a point of inflection at 50 per cent of ester decomposed. Konovalov (1887) proved that the accelerating effect in the Menshutkin reaction is due to the acetic acid formed and gave an equation for the reaction rate in the following form:

$$\omega = \frac{dx}{dt} = k (100 - x) \left( x + 2 \frac{1}{6} P \right)$$
 (12.38)

where x is the amount of ester decomposed in per cent; P is the initial concentration of acetic acid;  $2\frac{1}{6}$  is the ratio of the molecular weights of the ester and acid.

Konovalov's work was preceded by the work of Ostwald (1883) who had derived an equation for the rate of the hydrolysis of methylacetate ester in the presence of acetic acid added as a catalyst at the start of the reaction:

$$\frac{dx}{dt} = k (b + x) (a - x) \tag{12.39}$$

where a is the initial concentration of the ester; x is the amount of ester reacted; b is the initial concentration of acetic acid.

We shall now write the equation for an autocatalytic reaction in a somewhat different form, basing also on the hydrolysis of an ester, though this time it is the ethylacetate ester:

$$CH_3COOC_2H_5 + H_2O \longrightarrow CH_3COOH + C_2H_5OH$$

The processes of hydrolytic cleavage of esters of this kind are in general typical autocatalytic reactions. The catalyst is the acid formed, more exactly the hydrogen ions. In the presence of the preliminarily added strong acid the reaction is known to obey an ordinary first-order equation with a rate constant proportional to the concentration of the acid. Let a denote the initial concentration of the ester and x the amount of ester reacted and, hence, the amount of acetic acid formed. We shall further assume that in the initially neutral solution the reaction proceeds at a slow but finite velocity—the corresponding rate constant is  $k_0$ . We may assume, for example, the initial effect of hydrogen and hydroxyl ions, which are always present in aqueous solution. The overall rate equation is written in the form

$$w = \frac{dx}{dt} = k_0 (a - x) + kx (a - x)$$
 (12.40)

Here the first term on the right-hand side corresponds to the rate of the uncatalyzed reaction, and the second term to the rate of the catalyzed reaction, which is proportional to the concentration

of the catalyst, x. We shall first take a - x out of the parenthesis and then k; we get

$$w = \frac{dx}{dt} = k\left(\frac{k_0}{k} + x\right)(a - x) \tag{12.41}$$

Or, separating the variables,

$$\frac{dx}{\left(\frac{k_0}{k} + x\right)(a - x)} = k dt \tag{12.42}$$

The fraction must be decomposed into partial fractions and integrated. As a result, we arrive at the following relation between

the amount of substance reacted and the time:  $h_{k} \left[ a(k_{0}+k_{a}) t - 1 \right]$ 

$$x = a \frac{k_0 \left[ e^{(k_0 + ka)t} - 1 \right]}{ka + k_0 e^{(k_0 + ka)t}}$$
 (12.43)

As can readily be seen, x=0 at t=0 and at  $t\to\infty$  the terms ka and 1 may be neglected as compared with the infinitely increasing exponents of the function and then x=a. On the whole, however, the x=f(t) curve has a sigmoid character with a point

Amount of substance

reacted

tint time

Time

Fig. 12.9 The dependences of the amount of substance reacted on time:

1 and 2—for an autocatalytic reaction; 3—for a first-order reaction.

of inflection, which is typical of autocatalytic reactions. Differentiating x twice with respect to time and equating the derivative to zero, we find the time corresponding to the point of inflection:

$$t_{\inf} = \frac{\ln \frac{ak}{k_0}}{k_0 + ak} \tag{12.44}$$

It is evidently determined by the values of the rate constants and decreases with increasing rate constant of the catalyzed reaction. Figure 12.9 presents two curves showing the dependence of x on time for various values of k. As regards the extent of reaction corresponding to the point of inflection, it is practically independent of the values of the constants and is equal to half the initial amount. Indeed, substituting  $t_{\rm inf}$  from Eq. (12.44) into the initial formula for x (12.43) or, more simply, differentiating w with respect to x in expression (12.41), we get

$$x_{\text{inf}} = \frac{a}{2} - \frac{k_0}{2k} \approx \frac{a}{2}$$
 (12.45)

The term  $k_0/2k$  may apparently be ignored since by the condition the constant  $k_0$  is small as compared with k. The point of inflec-

tion on the reactant consumption curve evidently corresponds to the greatest reaction rate w—the slope of the curve dx/dt has a maximal value at this moment. It may be noted in this connection that the passage of the rate through a maximum at  $x \approx a/2$  is generally characteristic of autocatalytic reactions.

For comparison, Fig. 12.9 also gives curve 3 which corresponds to an ordinary, uncatalyzed first-order reaction—its course is monotonic and it has a constantly decreasing slope, i.e., with the rate which decreases from the initial moment. At a low initial rate of the reaction, for example, in the case represented by curve 2 in Fig. 12.9, there is scarcely any chemical change for some time during the early part of the reaction. In other words, the reaction proceeds with an induction period, the duration of which is associated with the accuracy of the analytical procedure employed.

Differentiation of x in expression (12.43) with respect to time t allows us to find the time dependence of the rate:

$$w = \frac{dx}{dt} = \frac{\left(\frac{k}{k_0} + \frac{1}{a}\right)(k_0 + ka) e^{(k_0 + ka) t}}{\left[\frac{k}{k_0} + \frac{1}{a} e^{(k_0 + ka) t}\right]^2}$$
(12.46)

Taking into account that  $ka/k_0 \gg 1$ , we can, at small t, neglect the exponent close to unity in the denominator. Then, introducing the notation for the constant quantities,

$$\frac{\left(\frac{k}{k_0} + \frac{1}{a}\right)(k_0 + ka)}{\left(\frac{k}{k_0}\right)^2} = A$$

and

$$k_0 + ka = \varphi$$

we obtain the following relation between the reaction rate and time for the early part of the reaction:

$$w = Ae^{\varphi t} \tag{12.47}$$

This expression is close to that derived for the rate of a branched-chain reaction (see page 259) also with no account taken of the consumption of the reactant. The kinetics of autocatalytic and branched-chain reactions happen to be closely related. Therefore, it is not always so easy to differentiate them during an investigation, though these reactions in general differ substantially by their nature. In reactions taking place in condensed systems, for example, in the decomposition of explosive substances, the autocatalytic acceleration of the process is often accompanied by acceleration due to heating.

#### 12.9. Induced Reactions. The Chemical Induction

We have already dealt with the so-called principle of independency (Chapter 3), according to which two or more reactions in a chemical system proceed independently of one another and each of them separately obeys the mass-action law. The overall reaction rate (the general change of the system) is summed up of the individual independent rates. It has also been pointed out that this fruitful principle, which is in fact one of the postulates of chemical kinetics, is not absolutely general. Many examples are known, which violate this principle, this being associated with the interplay of reactions, say, via a common intermediate or via the final product of one reaction, which acts as the catalyst for another reaction.

In this section we shall be concerned with so-called induced reactions—the phenomena of the acceleration of one reaction due to the occurrence of the other. Induced reactions were extensively studied by the Russian scientist N. Shilov, whose monograph is mainly used here.\* The term induced reactions was introduced by Ostwald in 1900, and the phenomenon itself was probably discovered by Kessler in 1855. As a rule, a distinction is made between the primary, spontaneous "inducing" process and the induced process, which does not proceed in the absence of the first. For example, tartaric acid does not react with chromic acid in dilute solutions but is readily oxidized if arsenous acid is simultaneously oxidized in the same medium. In this case, the reaction  $\text{CrO}_4^{2^-} + \text{As}_2\text{O}_3$  is the primary process and the reaction  $\text{CrO}_4^{2^-} + \text{C}_4\text{H}_6\text{O}_6$  is the induced reaction. In a general form, induced or coupled reactions may be written as follows:

I. 
$$A + B \longrightarrow \text{products}$$
 (the primary reaction)

II.  $A + C \longrightarrow \text{products}$  (the induced reaction)

Such reactions involve three substances at least; the substance A which participates in both reactions is called the actor. The substance B, the participation of which in the primary process induces the reaction between A and C, is called the **inductor**, and the substance C is the acceptor.

An important quantitative characteristic of induced or coupled reactions is the **induction factor**. It is defined as the ratio of the amount of the acceptor reacted to that of the inductor, expressed in moles or gram-equivalents, i.e., by definition, the induction factor

$$I = \frac{n_{\text{acc (C)}}}{n_{\text{ind (B)}}} \tag{12.48}$$

<sup>\*</sup> His name is also spelled Schilow (N. Schilow, Z. physik. Chem. Leipzig, 42, 641 (1903). — Tr.

indicates the number of moles or equivalents of the acceptor, which enter into reaction per unit amount of inductor reacted. It is precisely the fact that the inductor is continuously used up in order to induce a reaction that distinguishes induced reactions from catalyzed reactions—in catalysis the intermediate compounds or complexes are destroyed with the regeneration of the catalyst and the induction factor is equal to infinity in the case of ideal catalysis. Shilov himself formulated the difference between induced and catalyzed reactions in the following manner: "The rate of any chemical interaction may be expressed, as known, by a formula \* which is reminiscent of Ohm's law in appearance:

## reaction rate = $\frac{\text{driving force of the reaction}}{\text{passive resistance}}$

and since the driving force of the reaction is measured, generally speaking, by its free energy, then this expression indicates that the reaction rate of a chemical process is not exclusively dependent on the free energy which it can give off ...". "For the catalysis phenomena the elimination of passive resistance \*\* is the only possibility of explaining the accelerating effect: since the catalyst is not changed during the process, it cannot serve as a source of work and, hence, does not change the driving force of the reaction ...". "The situation is different with the phenomenon of chemical induction: owing to the fact that the inductor enters into the reaction, which proceeds arbitrarily (the primary process), and undergoes chemical change, the free energy liberated can compensate for the formation of a product, which requires the performance of work. Indeed, the oxidation by gaseous oxygen has been experimentally shown to produce ozone or hydrogen peroxide, which, other conditions being equal, have a larger reserve of free energy than the original oxygen ...". \*\*\*

It is presumed that induced reactions are quite widespread, especially in living organisms, but it is not always easy to differentiate them from catalyzed reactions in practice. We deal here mainly with induced oxidation reactions, in which the substance A in the above scheme (see page 360), i.e., the actor, is the oxidizing agent, since they have been most thoroughly investigated experimentally. A typical example is the oxidation by gaseous oxygen. Thus, arsenious acid does not react with oxygen under "ordinary conditions", but it is readily converted into arsenic acid

<sup>\*</sup> This formula was established by Ostwald and is an example of formal analogy.

<sup>\*\*</sup> The decrease of the activation energy in modern terminology.

\*\*\* N. Shilov, Induced Oxidation Reactions, A. M. Mamontov Publishers, Moscow, 1905 (in Russian).

if the oxidation is effected by sulphurous acid in the same medium:

I. 
$$2SO_2 + O_2 = 2SO_3$$
 (the primary reaction)

II. 
$$As_2O_3 + O_2 = As_2O_5$$
 (the secondary reaction)

Usually, the intermediate of the primary reaction in the oxidation by oxygen is hydrogen peroxide or other more complex peroxides. Not infrequently, they can be isolated and when the primary process is complete they can be used to oxidize the acceptor. The formation of an energetic oxidizing agent, hydrogen peroxide, possibly proceeds by the following scheme:

$$X + O_2 \longrightarrow XO + O$$
  
 $H_2O + O \longrightarrow H_2O_2$ 

A further example of reactions of this type is the oxidation of indigotin to isatin, which is coupled with the spontaneous oxidation of benzaldehyde:

$$C_6H_5CHO + O_2 \longrightarrow ...$$
 (the primary reaction) indigotin +  $O_2 \longrightarrow ...$  (the induced reaction)

Here the intermediate energetic oxidizing agent is evidently benzoyl peroxide. The largest induction factor in such reactions is equal to unity—the oxygen is distributed equally between the inductor and the acceptor. The theory of direct formation of peroxides in oxidations by gaseous oxygen was formulated by N. A. Bakh and was thoroughly elaborated by Engler.

In his experimental investigations Shilov employed the procedure that enables induced reactions to be distinguished from catalyzed reactions. If it is presumed that the inductor acts catalytically on the reaction between the actor and the acceptor, disappearing simultaneously in the independent reaction with the actor, then, assuming that both reactions are second order, we obtain the following kinetic equations:

$$-\frac{dc_{\rm acc}}{dt} = k_1 c_{\rm cat} c_{\rm acc}$$
 (12.49)

$$-\frac{dc_{\text{cat}}}{dt} = k_2 c_{\text{cat}} c_{\text{act}} \tag{12.50}$$

On the basis of these equations the quantity equivalent to the induction factor will be defined as follows:

$$I = \frac{c_{\text{acc}}^0}{c_{\text{cat}}^0} \left( 1 - e^{-\frac{k_1}{k_2} c_{\text{cat}}^0} \right)$$
 (12.51)

From this it follows that in this case I will increase with increasing ratio  $c_{\rm acc}^0/c_{\rm cat}^0$ . In the case of induced reactions the induction factor tends to a certain limiting value, corresponding to

the conditions when the inductor forms an intermediate compound which then becomes entirely involved in the interaction with the acceptor. As an example, we give the oxidation of sulphurous acid (inductor) and arsenious acid (acceptor) by bromic acid (actor), studied by Shilov:

The primary reaction  $HBrO_3 + SO_2$ The induced reaction  $HBrO_3 + As_2O_3$ 

Figure 12.10 is a plot of the values of I found experimentally versus the ratio of the acceptor and inductor concentrations.

As seen, I tends to a constant value equal to 2. It is most likely to assume the formation of an unstable oxidation state of

an inductor of the peroxide nature (as an intermediate), say, of persulphuric acid.

In other cases, such an unstable oxidation state can be formed only by the actor. For example, in the system HBrO<sub>3</sub> + HBr + + SO<sub>2</sub> the gradual regeneration of bromic acid with the transient formation of bromous and hypobromous acids and bromine is assumed.

In still other cases, it is possible that the intermediate is a complex compound consisting of:

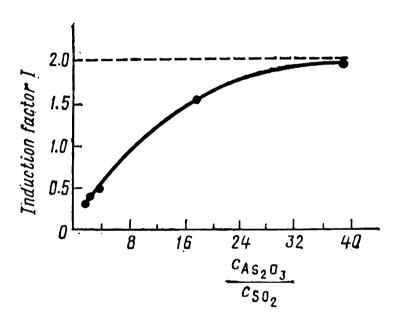


Fig. 12.10. The dependence of the induction factor on the ratio of the acceptor concentration to the inductor concentration (after N. A. Shiloy).

(a) the inductor and the acceptor—the induced oxidation of hydroxy acids with arsenious acid and antimony oxide:

(b) the inductor and the actor—the oxidation of ammonia oxychloride by permanganate:

Phenomena are also known, which indicate that induced (coupled) reactions can be made to turn into catalyzed reactions. Às has already been mentioned, this is possible in general "... in those cases where the intermediate, through which the primary process is tied up with the secondary process is formed by the inductor and where it is regenerated under the experimental conditions ..." (Shilov). Shilov studied the reaction of oxidation of sodium thiosulphate by potassium persulphate to give tetrathionate in the presence of the ferric and ferrous ions, Fe3+ and Fe2+. It has been shown that in the presence of Fe<sup>3+</sup> ions the reaction is catalyzed—its rate is directly proportional to the concentration of Fe3+ ions. The Fe2+ ions are considerably more active than Fe<sup>3+</sup> ions, but with ferrous ions there is no proportionality between the reaction rate and the concentration of ferrous salts. Retarding the catalysis by addition of acid or sodium fluoride, Shilov succeeded in demonstrating that for one Fe2+ ion there is oxidized one thiosulphate molecule. Thus, here we are dealing with a coupled (induced) oxidation of thiosulphate and the Fe2+ ion, which turns into the Fe<sup>3+</sup> ion and acts as a catalyst.

Let us now consider the phenomenon of **self-induction**, i.e., such induced reactions in which the *inductor concentration increases* during the course of the process. A requisite property of self-induced processes is the initial acceleration of the reaction and the passage of its rate through a maximum value. The initial acceleration is not, however, the property of self-induced processes alone. As we know, under isothermal conditions the end product may accumulate with acceleration in consecutive reactions (see Chapter 3, Sec. 3.3). Autocatalytic reactions, the kinetics of which have been already discussed (see Sec. 12.8), are also capable of being accelerated.

According to Shilov, the scheme of a self-induced reaction may be represented as follows:

1. The reactants first form certain intermediates, say A' and B'.

2. Then the intermediate A' interacts with one of the reactants, forming a new intermediate compound A''.

3. The new intermediate compound reacts with the other reactant to regenerate the first intermediate, i.e., A'.

On the whole, the scheme may be written thus:

$$(1) \quad A + B \longrightarrow A' + B'$$

$$(2) \quad A' + A \longrightarrow A''$$

(3) 
$$A'' + B \longrightarrow A' + B'$$

The first reaction is considered to be the slowest, rate-controlling step.

One of the self-induced reactions studied experimentally by Shilov is the oxidation of arsenious acid by bromic acid. It has

been found that the reaction  $HBrO_3 + As_2O_3$  is accelerated by hydrobromic acid; in the absence of HBr and in weakly acid solutions the reaction does not proceed at all. At a higher concentration of hydrogen ions the reaction starts spontaneously but has a distinct induction period. In this initial period there is formed a certain amount of HBr:

- (0)  $2HBrO_3 + 3As_2O_3 \longrightarrow 2HBr + As_2O_5$  (a very slow reaction) Further oxidation proceeds with the participation of the inductor HBr:
  - (1)  $HBrO_3 + HBr = HBrO_2 + HBrO$  (a slow reaction)
  - (2)  $4HBr + HBrO + HBrO_2 = 3Br_2 + 3H_2O$ (3)  $2Br_2 + As_2O_3 + 2H_2O = As_2O_5 + 4HBr$  } (fast reactions)

The inductor is formed in reactions (0) and (3) and used up in reactions (1) and (2). The entire process is self-induced since the inductor HBr and the energetic oxidizing agent  $Br_2$  are accumulated. Thus, the cause of the acceleration is the formation of a highly reactive intermediate ( $Br_2$ ) which disappears at the end of the reaction. This is what apparently constitutes the essential difference between self-induced reactions and autocatalytic and catalyzed reactions. In catalyzed reactions the accelerating agent is present in the system from the beginning and does not disappear when the reaction is completed. In autocatalytic reactions, a catalyst is produced in the course of the reaction as the end product, is accumulated and does not disappear either at the end of the reaction.

On the other hand, this may also be regarded as a similarity to the earlier discussed chain reactions, in particular, branchedchain reactions—in these reactions there are also accumulated active intermediates, which cause the reaction to accelerate. Of course, chain reactions, especially in the gas phase, have specific features of their own, which include the combustion limits, the generation of free radicals and biradicals during the course of the reaction, etc. The question whether the Shilov scheme is a chain reaction or not boils down to another question: Is the substance A' the end product (N. N. Semenov) or an active intermediate (N. S. Akulov)? There is no answer to this question regarding the overall scheme in the monograph by Shilov. In the concrete scheme of the reactions of oxidation of As2O3 by bromic acid, the end product IIBr takes part in the cycle 2-3. This is however hardly obligatory for the Shilov scheme; when he was writing his monograph, nothing was known about the existence of free atoms \* and radicals.

<sup>\*</sup> Though the "atomistic" oxygen, called "antozone" (the Schönbein theory), had already been mentioned in the literature.

The kinetic equations for self-induced reactions, given by Shilov, coincide with the equation for autocatalytic reactions. Namely, if the initial concentration of bromic acid is designated as a and its reduced amount as x, then

$$w = \frac{dx}{dt} = kx (a - x) \tag{12.52}$$

The reaction rate passes through a maximum at x = a/2. Since the equation in this form is inconvenient for experimental testing (at x = 0 the value of w is equal to zero and the reaction cannot be started), use is made in practice of the formula which is obtained when account is taken of the hydrobromic acid added in an amount b to the reaction mixture.

Then the reaction rate is expressed by the relation

$$w = \frac{dx}{dt} = k (b + x) (a - x)$$
 (12.53)

which on integration gives the formula

$$k = \frac{1}{t(a+b)} \ln \frac{a(b+x)}{b(a-x)}$$
 (12.54)

Equation (12.53) coincides with the Ostwald equation (12.42) for autocatalysis by the end product. In this connection, Shilov writes: "... in spite of this equation being outwardly identical with the Ostwald equation ..., its physical significance is quite different. The Ostwald equation implies a first-order process, in which one of the reaction products acts autocatalytically, exerting an influence only on the rate constant \*; the equation derived by me applies to a process, which is second order at least and which is accelerated by the end product owing to the inclusion of side reactions".\*\* This quotation from Shilov's monograph is given here in order to emphasize the somewhat mysterious influence of the catalyst "only on the rate constant". There arises the question as to how the catalyst can affect the rate constant, if it does not take part in the reaction, i.e., does not contribute to the occurrence of some side reactions facilitating the general course of the process. Apparently, the concrete scheme of the reactions in the oxidation of As2O3 by bromic acid is nevertheless the catalysis effected by the final product and the fact that the kinetic equations do coincide is not accidental.

Shilov also studied the "self-induced" process of oxidation of oxalic acid by potassium permanganate, in which the accelerating effect is exhibited by the Mn<sup>2+</sup> ions.

<sup>\*</sup> My italics (E. Yeremin).
\*\* N. Shilov, op. cit.

In concluding, we may broaden, to a certain extent, the concept of induced reactions and, while defining the induction factor by means of relation (12.48), use  $n_{acc}$  to denote the number of moles of the acceptor reacted additionally per  $n_{ind}$  moles of the inductor. In other words, in this case the primary reaction does proceed on its own and the role of the induced reaction is to involve an additional amount of the acceptor in the conversion. The concept of induced reactions in this formulation has also been applied to homogeneous gas reactions. For example, in the high-temperature pyrolysis of methane with ethane added it has been established that for one molecule of C<sub>2</sub>H<sub>6</sub> decomposed there react additionally two methane molecules, i.e., the induction factor is equal to 2. Here it is believed that ethane undergoes primary decomposition into two free methyl radicals, which then enter into reaction with the methane molecules. A similar phenomenon of "chemical induction" has been observed in the pyrolysis of methane in a highvoltage electric arc in the presence of propane and butane.

### 12.10. Fast Reactions in Solution \*

A considerable number of reactions have been dropped out of the scope of chemical kinetics until recently—they have been considered "instantaneous". They include numerous ionic reactions in solutions, say, the dissociation of water and the recombination of hydrogen ions (oxonium ions) and hydroxyl ions (hydroxide ions):

$$H_3O^+ + OH^- \implies 2H_2O$$

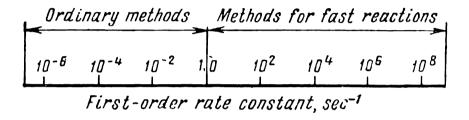
Methods of investigation have however been devised for the last several decades, which have enabled the range of measured rates to be considerably extended. For example, for first-order reactions the half-lives ( $T_{\frac{1}{2}}=0.693/k_1$ ) less than 10 seconds could not be accurately measured. Some new methods allow the half-life periods of the order of  $10^{-7}$  and even  $10^{-9}$  sec to be determined, i.e., the interval of measurable velocities is broadened by about 10 orders. The same is valid for second-order reactions. In the classical work of Bodenstein and Lind (see Chapter 3, Sec. 3.1) the rate constant of the decomposition of hydrogen iodide was measured within the range from  $4 \times 10^{-2}$  (781 K) to  $3.5 \times 10^{-7}$  litre  $\times$  mole<sup>-1</sup>·sec<sup>-1</sup> (556 K). Special methods worked out for fast reactions enable the kineticist to measure sufficiently reliably the rate constants amounting to  $10^{10}$  in the same units. Figure 12.11

<sup>\*</sup> For a more detailed treatment of the subject, the reader is referred to the monograph by E. E. Caldin (see the list of recommended literature at the end of the book).

is a pictorial representation of the ranges of reaction rates measurable by ordinary and special methods.

It may be said that no special theories are required in order to describe fast reactions. They come within the scope of the simple collision theory, though their activation energies are very small, amounting only to several (2-3) kilocalories per mole. The most rapid reactions occur apparently on each encounter \* of reactant molecules and their rate is limited only by diffusion.

A complete discussion of a large variety of existing methods of measuring fast reactions is not within the scope of this book; among these methods there are simple techniques based, for



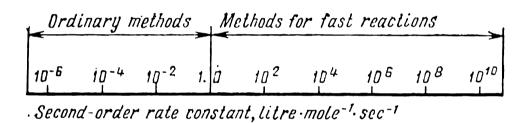


Fig. 12.11. Approximate ranges of rate constants measured by ordinary and special methods for fast reactions.

example, on the retardation of a reaction by decreasing the concentration of the reactants. When the reaction involves intensely coloured substances, then even small concentrations can be measured photometrically. This method has been employed to measure the rates of reactions in aqueous solution between Fe<sup>2+</sup> ions and the cobaltioxalate ions:

$$Fe^{2+} + [Co(C_2O_4)_3]^{3-} = Fe^{3+} + Co^{2+} + 3C_2O_4^{2-}$$

and also between the Fe³+ ion and the thiocyanate ion NCS-:

$$Fe^{3+} + NCS^{-} = FeNCS^{2+}$$

The rate constant of the first reaction exceeds 10<sup>4</sup> litre·mole<sup>-1</sup>·sec<sup>-1</sup>. In a number of cases, use can be made of the retardation of reactions by lowering the temperature. Rate measurements have been carried out in ethanol solutions at temperature down to

<sup>\*</sup> The number of encounters may be less than the number of collisions since the molecules that have encountered may collide several times, being trapped in the "cage" of solvent molecules.

-114 °C when the reaction proceeds by 106 times more slowly than at 25 °C. With isopentane, use has been made of temperatures as low as -140 °C. Low temperatures have also been employed in conjunction with other methods—flash photolysis or methods involving nuclear-magnetic-resonance or electron-paramagneticresonance spectra.

Of special methods used for fast reactions, mention should be made of the various flow methods: the continuous-flow method, the accelerated-flow method and the stopped-flow method. In particular, the stopped-flow and accelerated-flow methods have been used to measure the rate of the decomposition of hydrogen peroxide by the enzyme catalase. The second-order constant determined is

equal to about  $5 \times 10^7$  litre·mole<sup>-1</sup>·sec<sup>-1</sup>.

Let us consider in more detail the relaxation methods. The principle of these methods is as follows. The system which is at equilibrium is affected in some way—for example, the temperature or pressure is sharply changed. To the new conditions there corresponds a new state of equilibrium. It is however attained with some delay, which depends on the rates of the forward and reverse reactions. The time period during which the deviation from the equilibrium state decreases by e times \* is called the **relaxation** time: it is associated with the rate constants. We shall consider this relationship on simple examples.

Suppose that the reaction is first order in both directions, i.e.,

$$A \stackrel{k_1}{\rightleftharpoons} B$$

Suppose that the conditions in the system, which is initially at equilibrium, are sharply (practically "instantaneously") changed. To the new conditions there correspond the equilibrium concentrations  $\bar{a}$  and  $\bar{c}$ . At the time of observation t the instantaneous concentrations a and c still differ from the equilibrium concentrations by an amount x, i.e.,

$$x = a - \bar{a} = \bar{c} - c \tag{12.55}$$

The overall rate of the forward reaction leading to a state of equilibrium, is equal, at time t, to

$$-\frac{dx}{dt} = k_1 a - k_2 c ag{12.56}$$

We take into account the fact that at equilibrium the rates of the forward and reverse reactions are equal; then

$$k_1 \bar{a} - k_2 \bar{c} = 0 \tag{12.57}$$

<sup>•</sup> e is the base of natural logarithms.

and substitute the values of a and c from Eq. (12.55) into the rate expression (12.56). We obtain

$$\frac{dx}{dt} = (k_1 + k_2) x \tag{12.58}$$

Introducing then the overall first-order constant

$$k = k_1 + k_2 \tag{12.59}$$

and integrating relation (12.56) between limits from 0 to t and from  $x_0$  to x, we obtain the equation

$$x = x_0 e^{-kt} (12.60)$$

which describes the attainment of equilibrium. In this equation,  $x_0$  signifies the departure from the equilibrium concentrations immediately after the initial conditions are changed. The rate of attainment of equilibrium is determined by the constant k which is the sum of the rate constants of the forward and reverse reactions. When  $kt = k\tau = 1$ , then  $x/x_0 = 1/e$ , i.e., the difference between the instantaneous and equilibrium concentrations decreases by e times. This time interval  $\tau$  is called the relaxation time. Obviously,

$$\tau^{-1} = k = k_1 + k_2 \tag{12.61}$$

and the relaxation time is a quantity which is the inverse of the sum of the rate constants. In numerical value  $\tau$  is close to the half-life period  $T_{1/2}$  since

$$\frac{T_{1/2}}{\tau} = kT_{1/2} = \ln 2 = 0.693 \tag{12.62}$$

As known (see Chapter 2, Sec. 2.1), the inverse of any first-order rate constant is equal to the average life-time of reactant molecules under given conditions. Therefore, introducing the average lifetimes of the molecules A and B,  $\tau_A = 1/k_1$  and  $\tau_B = 1/k_2$ , we may write:

$$\tau^{-1} = \tau_{A}^{-1} + \tau_{B}^{-1} \tag{12.63}$$

Let us consider a reaction which is second order in the forward direction and first order in the reverse direction:

$$A + B \xrightarrow{k_1} C$$

The instantaneous concentrations of the reactants are denoted by a, b and c. The equilibrium concentrations corresponding to the new, sharply changed conditions, are designated by  $\bar{a}$ ,  $\bar{b}$ , and  $\bar{c}$ . At time t after the conditions are changed the instantaneous concentrations are still less than the equilibrium concentrations by

the amount x:

$$x = a - \bar{a} = b - \bar{b} = \bar{c} - c \tag{12.64}$$

The observed reaction rate at this moment is expressed by the difference between the rates of the forward and reverse reactions, i.e.,

$$-\frac{dx}{dt} = k_1 ab - k_2 c \tag{12.65}$$

which vanishes at equilibrium:

$$k_1 \bar{a} \bar{b} - k_2 \bar{c} = 0 \tag{12.66}$$

Expressing the instantaneous concentrations through x (12.64), employing also the equilibrium condition (12.66) and neglecting  $x^2$  because of the small displacement, we may write the reaction rate as follows:

$$-\frac{dx}{dt} = [k_1 (\bar{a} + \bar{b}) + k_2] \bar{x}$$
 (12.67)

Obviously, that for the given experiment the bracketed term is constant and may be regarded as a first-order rate constant \*(k) of the equation describing the approach of the system to equilibrium. The relaxation time is defined, as before, as the inverse of k:

$$\tau^{-1} = k = k_1 \left( \bar{a} + \bar{b} \right) + k_2 \tag{12.68}$$

In order to determine the rate constants  $k_1$  and  $k_2$ , one should find experimentally the value of  $\tau$  for a number of concentrations  $\bar{a} + \bar{b}$  and calculate the rate constants from the straight-line dependence obtained. If the equilibrium is strongly shifted to the right, as, for example, in the neutralization reaction

$$H_3O^+ + OH^- \xrightarrow{k_1 \atop k_2} 2H_2O$$

the constant  $k_2$  is negligibly small and Eq. (12.68) simplifies to

$$\tau^{-1} = k_1 (a + b) \tag{12.69}$$

In the practical utilization of relaxation methods, use is made of various experimental procedures. In the **temperature-jump method**, for example, the temperature of the ionic solution is sharply changed by discharging the capacitor which is charged to a voltage of the order of 100 kV. Thus, during the time of about 10<sup>-6</sup> sec it is possible to raise the temperature by 2-10°. The subsequent establishment of equilibrium is followed by means of various methods: by recording the change of electrical conductivity by

<sup>\*</sup> At small displacements.

means of a bridge circuit, incorporating an oscillograph, by recording photometrically the change of the colour of the reactants or of the indicator added and by other sufficiently rapid methods.

In the electron-pulse technique, use is made of the superimposition of an electric field, which increases the degree of dissociation of a weak electrolyte. Relaxation methods also include various techniques associated with the absorption of ultrasonic vibrations. The methods described have been used to measure the rates of one of the fastest reactions—the recombination of hydrogen ions and

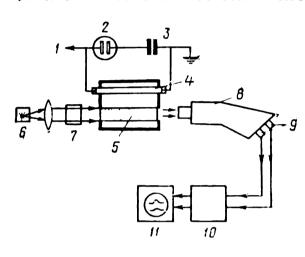


Fig. 12.12. Block diagram of apparatus for study of kinetics by flash photolysis (after Bridge and Porter):

1—to the high-voltage source (ca. 10 kV); 2—trigger; 3—capacitor; 4—flash lamp; 5—reaction vessel; 6—source of monochromatic light; 7—light filter; 8—spectrograph; 6—photomultipliers; 10—amplifiers; 11—oscillograph.

hydroxyl (hydroxide) ions. The dissociation constant and its temperature dependence for this reaction are well known and  $k_2 \ll k_1$ . Therefore, according to Eq. (12.69),

$$k_1 = \frac{1}{\tau \left( \left[ \text{OH}^- \right] + \left[ \text{H}_3 \text{O}^+ \right] \right)}$$

Table 12.6 lists the results of measurements of the rates of this reaction and some other reactions involving the proton transfer.

Methods that make use of relaxation include flash photolysis. The apparatus employed is schematically shown in Fig. 12.12. The system is brought out of equilibrium by means of an extremely intense flash of light from a special photoflash lamp, and then the return of the system to equi-

librium is followed. Thus, illuminating a solution of iodine with a flash of light can cause the dissociation of its molecules into their atoms:

$$I_2 \xrightarrow{hv} I + I \xrightarrow{k} I_2$$

Immediately after the flash the concentration of undissociated molecules is measured photometrically, using their ability to absorb light in the visible region and the fact that the atoms do not exhibit this ability. As known (see Chapter 8, Sec. 8.6), in the gas phase the recombination of iodine atoms is a third-order reaction—the participation of a third body is required. The activation energy is close to zero. In solution, where the solute is surrounded by the solvent molecules, which are ready to accept extra energy, no special third body is required and the reaction proceeds by second-order kinetics. According to the measurements carried out by Wallard in  $CCl_4$  at  $25\,^{\circ}C$ ,  $k = (6.9 \pm 0.6) \times 10^9$  and at  $50\,^{\circ}C$  the value of  $k = 1.03 \times 10^{10}$  litre-mole<sup>-1</sup>-sec<sup>-1</sup>. These values

TABLE 12.6. The Reactions of Hydrogen and Hydroxyl Ions. The Second-Order Rate Constant k (litre-mole<sup>-1</sup>·sec<sup>-1</sup>) in Water

Ion	Reagent	Method	t, °C	k
$H_3O^{\dagger}$	OH-	Temperature-jump	23	$(1.3\pm0.1)\times10^{11}$
J	Phenol red		13	$3 \times 10^{11}$
	Chlorophenol red		13	$2.3 \times 10^{11}$
OH	Cresol red		-	$4 \times 10^9$
	Phenolphthalein		-	$1 \times 10^9$
H <sub>2</sub> O <sup>+</sup>	OH-	Electron-pulse	25	$(1.4\pm0.2)\times10^{11}$
	SH <sup>-</sup>		25	$(7.5\pm1)\times10^{10}$
	F <sup>-</sup>		25	$1 \times 10^{11}$
OH-	NH;		20	$(3.3\pm0.3)\times10^{10}$
011	CH₃NH₃⁺		20	$3.7\times10^{10}$
H,O <sup>+</sup>	SO <sub>4</sub> -	Ultrasonic absorp- tion	_	$(1\pm0.5) \times 10^{11}$
	HSO <sub>3</sub>	11011	20	$2 \times 10^8$
OH-	NH <sup>+</sup>		20	$3 \times 10^{10}$
	1114			

are close to the rate constant of the diffusion-controlled reaction between the uncharged molecules ( $k_D \approx 10^{10}$ ). The activation energy calculated from the given values of k ( $E_A = 3.2 \, \text{kcal/mole}$ ) practically coincides with the value found for the diffusion of iodine in carbon tetrachloride. Thus, under these conditions the molecule is formed on each encounter of the atoms.

The rate of recombination of iodine atoms in solutions has also been determined by more ordinary photochemical methods. The results obtained are presented in Table 12.7.

As can be seen, this method too gives the value of k of the order of  $10^{10}$  litre·mole<sup>-1</sup>·sec<sup>-1</sup>. If the reaction involves free radicals, a study of electron-paramagnetic-resonance (EPR) spectra may prove to be effective in the investigation of kinetics, EPR being a phenomenon associated with the presence of an unpaired electron on radicals. Such an electron may be tentatively regarded as a rotating charged body with a certain quantized momentum (the quantum number called the spin is equal to 1/2). Related with the rotating charge is the magnetic moment directed along the axis of rotation. In a strong external magnetic field the mo-

Solvent	k, litre/mole <sup>-1</sup> ·sec <sup>-1</sup> · $10^{-9}$		
Hexane	13.1±1.6		
Carbon tetrachloride	$8.2 \pm 2.1$		
1,3-Hexachlorobutadiene	$6.1 \pm 1.2$		
Flash photolysis Carbon tetrachloride	6.9±0.6		
Carbon tetracinoride	0.9±0.0		

TABLE 12.7. The Recombination of Iodine Atoms in Solutions at 25°C

ment is oriented either along or counter to the field. These two orientations differ in energy. Thus, in the magnetic field the electron can occupy two energy levels. It can be made to move from one energy level to another by superimposing a second, considerably weaker field which varies with a certain resonance frequency. If the components of the magnetic moment of the electron are equal to  $+\mu$  and  $-\mu$ , the energies of the orientation in a field of intensity H will be equal to  $-\mu H$  and  $+\mu H$ . The electrons of a substance are classified into two groups with energies differing by  $2\mu H$ . In a state with a lower energy there are more electrons since in a thermal equilibrium the ratio of the numbers of electrons is defined by the Boltzmann law:

$$\frac{n_{\text{upper}}}{n_{\text{lower}}} = e^{-\frac{\Delta \varepsilon}{kT}} \tag{12.70}$$

Here  $\Delta \varepsilon = 2\mu H \ll kT$  and in a typical case this ratio is equal to 0.998.

In resonance with a variable magnetic field having a frequency of  $v = 2\mu H/h$  there is observed a maximum of energy absorption. As seen, the resonance frequency is proportional to the strength of the principal magnetic field. Therefore, in studying absorption EPR spectra, it is more convenient, with the frequency of electromagnetic radiation kept constant, to attain resonance by changing the principal magnetic field strength H. With an applied field of H = 3000 gauss the resonance frequency is close to  $10^{10}$  sec<sup>-1</sup>. This corresponds to the wavelength of electromagnetic radiation in the microwave region of  $\lambda \approx 3$  cm. When an electron interacts with a proton, which also has a spin of I = 1/2, or with other nuclei with spin I the energy levels may be split: then in the EPR spectrum there will be observed not one but several absorption peaks. By means of observations of this fine or even superfine structure of the EPR spectra it is sometimes possible to identify radicals. On the other hand, by studying the conditions of disappearance of the fine structure we can determine the average lifetime of radicals, i.e., in the long run, the velocity with which they

disappear for some reason or other.

The average lifetime of a radical  $(\tau)$  is associated with the width of the absorption line in the EPR spectrum. At this point, there might be useful to draw an analogy with optical spectroscopy where the intrinsic width of the light absorption line is determined by the uncertainty of the energy of the upper excited state of the molecule,  $\epsilon$ . This uncertainty is specified by the Heisenberg principle:

$$\delta \varepsilon \cdot \delta t \equiv \frac{h}{2\pi} \tag{12.71}$$

where  $\delta\epsilon$  is the interval of energy values, and  $\delta t$  may be identified with the average lifetime  $\tau$  of molecules in an excited state. Since the ground state is, as a rule, stable,  $\tau \approx \infty$  and  $\epsilon'$  is single-valued, the uncertainty of the energy of the upper level specifies the width of the observed line:

$$\delta v = \delta (\epsilon'' - \epsilon')/h = \delta \epsilon'/h = \frac{1}{2} \pi \tau'' \operatorname{sec}^{-1}$$
 (12.72)

Here  $\epsilon''$  and  $\epsilon'$  are the energies of the excited and ground levels;  $\tau''$  is the mean lifetime of the excited level. For the light absorption line in the visible region with a width of  $\delta\lambda=0.001$  Å, the value of  $\tau''$  is equal to  $10^{-8}$  sec—this is the "ordinary" mean lifetime of the electronically excited states of the molecule.

In EPR spectra the width of the absorption line is associated with the uncertainty of the energy values for an electron in both states. However, in this case too the line width may be tied up with the mean lifetime of a radical as a whole. This has the following relationship to kinetics. In the absence of a reaction, say, at low temperatures, there is observed a narrower sharp line. When the reaction takes place, the line is broadened since the average lifetime of the radical is shortened.

Good examples of the kinetic use of EPR spectra are the investigations of liquid sulphur and naphthalene ions. Sulphur is known to melt at 119 °C. On heating up to about 160 °C its viscosity increases, reaching a maximum at about 178 °C. The EPR spectrum is a single line which is broadened from 40 gauss at 200 °C to 100 gauss \* at 414 °C. These changes and the EPR spectrum are associated with the opening of the S<sub>8</sub> ring and with the formation of a more or less long polymer diradical:

$$S_8 \rightleftharpoons -S(S_n)S-$$

<sup>\*</sup> Since the maximum of absorption of electromagnetic oscillations is attained by changing the field strength, the line width can also be measured in field strength (induction) units.

The broadening of the absorption line should be tied up with the decrease of the average lifetime of the biradicals (the depolymer-

ization process); it has been found that  $\tau \approx 10^{-9}$  sec.

A specific feature of the kinetic uses of EPR spectra (and also of nuclear magnetic resonance or NMR spectra) is the possibility of measuring reaction velocities (with the participation of radicals) at equilibrium. Here exchanges of electrons become important. If an ether solution of naphthalene is treated with sodium, there will be formed paramagnetic naphthalene ions  $C_{10}H_8$ , which also give a characteristic EPR spectrum. Upon addition of naphthalene to such a solution the absorption lines are broadened, i.e., the average lifetime of the ion is shortened. It is presumed that this is associated with an exchange process of the type

$$C_{10}H_8^- + C_{10}H_8 \implies C_{10}H_8 + C_{10}H_8^-$$

If k is the rate constant, then the rate of the reaction in any direction will be given by

$$w = -\frac{d[N]}{dt} = k[N^-][N]$$

It has been established that at 30-35 °C the rate constant depends on the cation species  $(K^+, Na^+, Li^+)$  and the solvent and its values lie within the range of  $10^7$  to  $10^9$  litre·mole<sup>-1</sup>·sec<sup>-1</sup>.

In conclusion, let us consider the application of nuclear magnetic resonance (NMR) spectra. Any compound, whose molecules contain a nucleus with spin, a proton, the ordinary isotopes of N and F, the less widespread isotopes of C and O (but not <sup>12</sup>C and <sup>16</sup>O), can give NMR spectra. In other words, a substance having such nuclei can, while residing in a sufficiently strong magnetic field, absorb electromagnetic radiation possessing a resonance frequency. The theory of NMR spectra is closely related to the theory of EPR spectra, but the resonance frequencies defined by the relation

$$hv = 2\mu H$$

differ considerably from the EPR frequencies. Thus, for example, for protons the magnetic moment  $\mu = 1.42 \times 10^{-23} \text{ erg} \cdot \text{gauss}^{-1}$  and is about 657 times less than that of an electron. With a field of  $H = 10^4$  gauss the resonance frequency  $\nu = 4.96 \times 10^7 \text{ sec}^{-1}$ , which corresponds to the wavelength  $\lambda = 10^3 \text{ cm}$  or 10 m, which is in the radiofrequency range.

Compounds in which all the hydrogen atoms are equivalent and which contain no nuclei with a magnetic moment, for example, ordinary water or benzene, give a single proton resonance line. But, for example, in the alcohol CH<sub>3</sub>CH<sub>2</sub>OH there are three non-equivalent hydrogen atoms in the groups CH<sub>2</sub>, CH<sub>3</sub> and OH. The

electron environments are different for these atoms and with an instrument of medium resolution the absorption line is split into three lines—there are observed so-called chemical shifts. When the protons are non-equivalent, their interaction via the electrons of molecules is also possible. This is known as the spin-spin coupling which leads to an additional splitting of the energy levels of the protons and to the appearance of a superfine structure in the spectrum. By determining the shape and width of the absorption lines in the proton resonance spectrum and also their change caused by the conditions, say, the temperature and the amount of the reference substance added, it is possible to arrive at the rate of some reactions. Thus, the broadenings of the proton line of water in the presence of alcohol under the action of acid and base added have been interpreted with the aid of the following exchange reactions:

(1) ROH + OH 
$$\stackrel{k_1}{\Longleftrightarrow}$$
 RO + H<sub>2</sub>O  $k_1 = 2.8 \times 10^5$  litre·mole -  $^1$ ·sec- $^1$  or

$$ROH' + HOH + RO^{-} \rightleftharpoons RO^{-} + HOH' + ROH$$

(2) 
$$ROH + RO^{-} \rightleftharpoons RO^{-} + ROH \qquad k_2 = 1.4 \times 10^6$$

(3) ROH + H'OH 
$$\stackrel{k}{\Longleftrightarrow}$$
 ROH' + HOH  $k_3 = 0.8$ 

(4) 
$$ROH + H_3O^+ \stackrel{k_1}{\iff} ROH_2^+ + H_2O$$
  $k_4 = 2.8 \times 10^8$ 

or

$$ROH + H'OII + ROH_2^+ \implies ROH'H^+ + HOH + ROH$$

(5) 
$$ROH' + ROH_2^+ \stackrel{k_-}{\Longleftrightarrow} ROH'H + ROH \quad k_5 = 1 \times 10^8$$

The intrinsic line of water becomes narrower in the presence of acids and bases. This happens because of the so-called "fast" exchange, which causes the "exchange narrowing" at 25 °C:

$$H_2O + H_3O^+ \stackrel{k_1}{\rightleftharpoons} H_3O^+ + H_2O$$
  $k_1 \approx 1.1 \times 10^{10} \text{ litre} \cdot \text{mole}^{-1} \cdot \text{sec}^{-1}$   
 $H_2O + OH^- \stackrel{k_2}{\rightleftharpoons} OH^- + H_2O$   $k_2 \approx 5.5 \times 10^9 \text{ litre} \cdot \text{mole}^{-1} \cdot \text{sec}^{-1}$ 

There have also been developed photochemical, fluorescence and electrochemical methods of measuring reaction rates.

The Theory of Fast Reactions. As calculations show, the kinetics of many fast (but not very fast) reactions are described by formula (7.12) of the simple collision theory of bimolecular reactions:

$$k = z_0 e^{-\frac{E}{RT}}$$

Here  $z_0$ , the frequency factor, has, as a rule, a value close to the "normal" value:

$$z_0 = 2.8 \times 10^{11} \text{ litre} \cdot \text{mole}^{-1} \cdot \text{sec}^{-1}$$

[see Eq. (7.17)], and E is the energy of activation. The reaction proves to be fast due to the small value of the energy of activation. The effect of the change of E at constant  $z_0$  on the rate constants can be traced out from the values of k calculated by the equation  $k = 10^{11}$  exp (-E/RT) for different values of E at 25 °C:

E, kcal·mole<sup>-1</sup> 14 12.5 10 7 4 (0)  
k, litre·mole<sup>-1</sup>·sec<sup>-1</sup> 10 
$$10^2$$
  $10^1$   $10^6$   $10^8$  (10<sup>11</sup>)

The last numbers are enclosed in parentheses because at zero energy of activation the reaction rate is thought to be controlled by diffusion and the activation energy, though small but still different from zero, must correspond to the diffusion process. Rate constants of the order of  $10^{10}$  litre·mole<sup>-1</sup>·sec<sup>-1</sup> are interpreted as limiting values determined by the frequency of encounters between the reactant molecules as a result of the diffusion occurring in solution. For a solution containing uncharged particles A and B it may be shown, using Fick's law (the rate of diffusion is proportional to the concentration gradient), that the number of collisions between A and B per 1 ml per second is equal to

$$w = 4\pi (D_{A} + D_{B}) (r_{A} + r_{B}) n_{A} n_{B}$$
 (12.73)

Here w is the reaction rate equal to the number of collisions and expressed by the number of molecules reacted in 1 ml per second;  $D_{\Lambda}$  and  $D_{B}$  are the diffusion coefficients for molecules A and B; and  $r_{\Lambda}$  and  $r_{B}$  are their radii. Obviously, the factor before the product of the concentrations is the reaction rate constant of the diffusion-controlled reaction  $(k_{D})$ . Thus,

$$k_D = 4\pi (D_A + D_B) (r_A + r_B) \text{ ml} \cdot \text{molecules}^{-1} \cdot \text{sec}^{-1}$$
 (12.74)

In order to convert to conventional units, we multiply by Avogadro's number and divide by 1000:

$$k_D = \frac{4\pi N_A}{1000} (D_A + D_B) (r_A + r_B) \text{ litres} \cdot \text{mole}^{-1} \cdot \text{sec}^{-1}$$
 (12.75)

From this equation we may eliminate the diffusion coefficients, expressing them with the aid of the Stokes-Einstein equation in terms of the solvent viscosity and the radii:

$$D_{\rm A} = \frac{kT}{6\pi\eta r_{\rm A}}, \quad D_{\rm B} = \frac{kT}{6\pi\eta r_{\rm B}} \tag{12.76}$$

Now we obtain

$$k_D = \frac{2N_A kT}{3000\eta} \cdot \frac{(r_A + r_B)^2}{r_A \cdot r_B} \text{ litres} \cdot \text{mole}^{-1} \cdot \text{sec}^{-1} = \frac{2RT}{3000\eta} \cdot \frac{(r_A + r_B)^2}{r_A \cdot r_B}$$
 (12.77)

Calculations show that the difference in the radii is not significant; therefore, putting  $r_A = r_B$ , we obtain the following simple expression:

$$k_D = \frac{8RT}{3000\eta} \text{ litre} \cdot \text{mole}^{-1} \cdot \text{sec}^{-1}$$
 (12.78)

According to relation (12.78), the rate constant of the diffusioncontrolled reaction must be inversely proportional to the viscosity of the solvent, and the energy of activation must coincide with the activation energy of viscous flow, i.e., must be small as compared with the activation energies of ordinary reactions. All this is approximately consistent with experiment. For example, in water at 25 °C the viscosity  $\eta \approx 0.01$  poise and  $k_D = 0.7 \times 10^{10} \, \text{litre·mole}^{-1} \cdot \text{sec}^{-1}$ , and in benzene and chloroform the values of  $k_D$  are, respectively, equal to  $0.95 \times 10^{10}$  and  $1.05 \times 10^{10}$  litre·mole<sup>-1</sup>·sec<sup>-1</sup>. These values are all close to the values experimentally observed for very fast reactions of uncharged particles. For instance, as seen from Table 12.8, the rate constant for the recombination of iodine atoms has values of the order of 10<sup>10</sup> litre⋅mole<sup>-1</sup>⋅sec<sup>-1</sup> in different solvents. The numerical values of the activation energy for reactions, the rate of which is limited by diffusion, must lie within the range 1-3 kcal/mole in the case of ordinary solvents and small molecules ( $r \approx 10^{-8}$  cm). This is also consistent with experiment. If the experimentally observed activation energy is greater than 6 kcal/mole, diffusion ceases to be the controlling factor and activated collisions, the number of which is calculated by the ordinary formula (7.12), come into play. With the "normal" value of the pre-exponential factor this corresponds to rate constants less than 107 litre mole -1 · sec-1.

If the reacting particles A and B are ions, Eq. (12.78) should be modified in order to take into account the effect of the electrostatic forces. According to Debye,

$$k_D = \frac{8RT}{3000\eta} \cdot \frac{\delta}{e^{\delta} - 1} \tag{12.79}$$

where

$$\delta = \frac{Z_{\rm A} Z_{\rm B} e^2}{\varepsilon k T a}$$

Here e is the charge on the electron;  $Z_A$  and  $Z_B$  are the multiplicities of ionic charges;  $\varepsilon$  is the dielectric constant of the solvent; and a is the distance of approach of the ions  $(r_A + r_B)$ , required for the reaction to occur.

As can be seen from Table 12.8, the values of the additional factor are less than unity for ions of like charge (forces of repulsion!) and greater than unity for ions of opposite charge; they are also significantly dependent on the adopted distance of nearest

TABLE 12.8. The Values of the Factor  $\delta/(e^{\delta}-1)=\frac{k_{\rm D~(ions)}}{k_{\rm D~(molecules)}}$  in the Rate Constant of the Reaction Between lons with the Charge Multiplicities  $Z_{\rm A}$  and  $Z_{\rm B}$  for Various Distances a. Water at 25 °C

$z_{A} z_{B}$	$k_{\rm D~(ions)}/k_{\rm D~(imolecules)}$ at various values of a. Å			
-V -R	2.0	5.0	<b>7.</b> 5	10.0
+2	0.005	0.17	0.34	0.45
+2 +1 -1 -2	0.10	0.45	0.60	0.69
<u>-1</u>	3.7	1.9	1.6	1.4
<b>—</b> 2	7.1	3.0	2,2	1.9

approach of ions, a. In connection with this latter quantity, it will be interesting to return once again to the neutralization reaction  $H_3O^+ + OH^-$ . It may be regarded as belonging to the category of the most rapid reactions—its rate constant in water, as seen from Table 12.8, is  $1.4 \times 10^{11}$  litre·mole<sup>-1</sup>·sec<sup>-1</sup>. As suggested by Eigen, the rate constants  $k_D$  calculated by Eq. (12.79) for different values of a agree most satisfactorily with the listed experimental values at a ranging from 6 to 8 Å. Since this distance corresponds to 2-3 internuclear separations in the hydrogen bond, we may conclude that reactions of this type proceed by a special mechanism. No proton transfer (in the direct sense) occurs in these reactions; what takes place is simply a shift of the proton along the hydrogen bond without removal of the solvation shell. In a general case, with the participation of the anion  $A^-$ , this mechanism may be represented as follows:

Solvated Ion A

or, with the participation of a hydroxyl ion,

Solvated ion HA+

Very fast proton-transfer reactions are evidently the only reactions in which the departure from classical behaviour can be detected, namely, the manifestation of the quantum-mechanical tunneling effect. What is meant here is the probability that the particle will

overcome the energy barrier even if its energy is less than the height of the barrier. The point is that for a proton the de Broglie wavelength  $\lambda = h/mv$  has the largest value as compared with other atoms. At ordinary temperatures they are equal to 1-2 A and may prove to be of the same order of magnitude as the width of the energy barrier. For example, the following manifestation of the tunneling effect in kinetics is predicted. Above room temperature the plot of  $\log k$  versus 1/T will be nearly linear in accordance with the Arrhenius equation. As the temperature decreases the plot will deviate from the straight-line course in such a way that the observed rate will increasingly exceed the rate calculated by the Arrhenius equation. This is associated with the decrease of the fraction (or number) of molecules possessing an energy higher than the barrier and, hence, with the increase of the fraction "penetrating" through the barrier. A rather large number of cases involving curvature of the Arrhenius plot have been detected up to the present time. It is possible that part of them are due to the quantum-mechanical tunneling effect.

# Kinetics of Topochemical Reactions

### 13.1. General Description of Topochemical Reactions

Under the heading of topochemical reactions should be included numerous processes which involve one solid substance at least among the reactants and also the products. First there are a large number of reactions of decomposition of solids of the type:

A (solid) 
$$\longrightarrow$$
 B (solid)  $+$  G (gas)

For instance, the dehydration of crystal hydrates

$$CuSO_4 \cdot 5H_2O \longrightarrow CuSO_4 \cdot 3H_2O + 2H_2O$$
 (vapour)

or the reaction of lime burning

$$CaCO_3 \longrightarrow CaO + CO_2$$

Second, there are reactions between a solid and a gas, which may or may not result in the formation of gaseous products:

$$A (solid) + B (gas) \rightarrow C (solid) + [D (gas)]$$

An example of such a reaction is the reduction of ferrous oxide

$$FeO + CO \longrightarrow Fe + CO_2$$

which plays a great part in metallurgy.

Third, mention should be made here of the versions of reactions of the types listed, in which a liquid is involved instead of a gas.

All these reactions have one specific feature in common—the process is proceeding at the interface between two solid phases, the reactant and the product. The name of the reactions under discussion stems from the Greek word topos meaning "place" or "site". The indicated specificity of topochemical reactions gives rise to special kinetics which have features common to all the types of reactions indicated; therefore, these reactions may be classified into a special class of reactions.

Here we shall consider reactions of the first type, i.e., processes involving the thermal decomposition of solids; however, the common features of these processes may be extended, with a certain degree of reliability, to other types of topochemical reactions.

For topochemical reactions the definition of the reaction rate (1.4) or (1.5) is not suitable since the process takes place neither in the volume nor in the bulk of the substance but at the interface between the phases. It is for this reason that the reaction rate is defined as the change in time of the degree of conversion (the

extent of reaction), i.e., the reaction rate is given by

$$w = d\alpha/dt \tag{13.1}$$

where  $\alpha = (N_0 - N)/N_0$  if  $N_0$  is the reactant and N the instantaneous amount of the reactant.

Figure 13.1 gives generalized curves, the portions of which have been observed in studying individual reactions of decomposition of solids. The solid curve expresses the dependence of the extent of reaction on time from the start of the reaction (the reaction is conducted under isothermal conditions as far as possible). The following portions of the curve

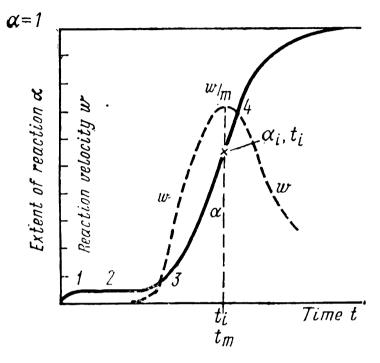


Fig. 13.1. The generalized (master) curves for topochemical reactions:

The solid curve is the dependence of the extent of decomposition on time; the dotted curve is the dependence of the reaction rate on time.

can be distinguished. The portion I corresponds to the rapid initial evolution of the gas, which is most frequently caused by the desorption of the gas adsorbed physically on the surface of the solid. In isolated cases, there may also occur the initial surface decomposition of the substance. The portion I is the induction period during which the reaction either does not occur at all or proceeds very slowly. The induction period is followed by the acceleratory portion I which ends at the point of inflection of the curve I curve I in the extent of reaction often reaches a value of I is the induction of the retardation of the reaction nearing its completion. On the whole, we may say that the function I is a sigmoid curve characteristic of autocatalytic reactions (Fig. 12.9) or of reactions in which the final product is formed via intermediate steps (consecutive reactions, Fig. 3.1).

The dotted curve in Fig. 13.1 shows the dependence of the reaction rate ( $w = d\alpha/dt$ ) on time. It is clearly seen that the reaction rate increases and reaches a maximum at time  $t_m = t_i$ .

It should also be noted that Fig. 13.1 presents generalized curves (called master curves), with all the portions observed in

reactions of decomposition of solids. Such master curves are obtained, for example, for the decomposition of lithium aluminium hydride, LiAlH<sub>4</sub>, and mercury fulminate,  $Hg(ONC)_2$ . For other processes of decomposition of various solids certain portions of the curves may be absent. For example, the period of initial gas evolution (portion 1) is often found to be missing. Not infrequently, cases are observed, where portions 1, 2, and 3 are absent, and the reaction proceeds from the start with the greatest velocity; as an example may be cited the decomposition of magnesium hydroxide and silver azide. But in such cases it may be presumed that the initial periods 1, 2, and 3 are very short, which makes them practically non-observable.

### 13.2. Mechanism of Topochemical Reactions

At present there are no generally adopted theories of topochemical reactions and, accordingly, there are no topokinetic equations suitable for the description of all the steps of decomposition reactions. Therefore, we shall confine ourselves to the consideration of the most reliable and most widely accepted conceptions. These include the concept of the development of the reaction only on the interface between two solid phases, the reactant and the product, which was first proposed by Langmuir (1916) in connection with the reaction

$$CaCO_3 \longrightarrow CaO + CO_2$$

In 1925 McDonald and Hinshelwood formulated the concept of the development of a topochemical reaction by way of the formation and growth of reaction nuclei—the nuclei of the solid product. The essential feature of this concept is the increase of the interfacial area at the first stage of the reaction with the attending increase of the rate.

According to Fraenkel and Getz (1925), the conversion starts at separate points—nuclei that are formed on the crystal surface, which is evidently associated with the various types of imperfections of the crystal lattice. In the simplest case, these may be, for example, misfit dislocations climbing to the surface, vacancies, accumulations of atoms (ions) in the interstices, etc. These structural units or elements of the crystal lattice are characterized by an increased free energy and, hence, they exhibit higher reactivity. The nuclei are also called **potential nucleating centres**.

Figure 13.2 is a pictorial representation of the development of the reaction in crystals. The growth of nuclei, spherical nuclei in this case, begins near the surface nuclei. As the reaction proceeds the surface of the nuclei, i.e., the interface between the reactant and the solid product, increases, as a result of which the reaction is accelerated. When the nuclei merge, the surface area increases to its largest size and the reaction rate reaches a maximum. Then the reaction slows down. This picture may be considerably complicated by the cracking of the crystals, which is attributed, in the first place, to the difference in the specific volumes of the initial phase and the new phase.

Mention should also be made of the scheme proposed by Garner in 1933 to account for the initial acceleration of the reaction  $[\alpha = \exp(kt)]$ : the model of linear branched chains. The reaction also begins at some sites on the surface, from which thin filaments of the product grow. The growth continues until the filaments come across one of the cracks in the crystal lattice,

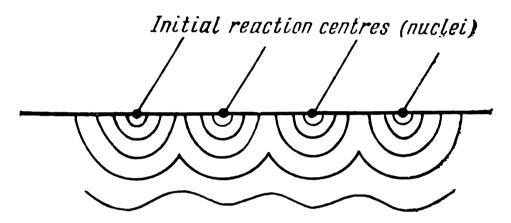


Fig. 13.2. The development and merging of spherical nuclei of the solid product in a topochemical reaction.

where branching, i.e., the formation of new filaments, occurs. According to the later version of these conceptions, the development of such chains takes place only on the surface, and the growth of compact bulk nuclei begins at the branching points.

From the brief outline given above it must be clear that the kinetics of the reaction depend on many factors (which are not always even accessible to consideration), primarily on the law of nucleation, i.e., the generation of potential reaction centres, and on the law of growth of the nuclei.

In this connection let us first consider some possible versions of the laws of nucleation.

Thus, the instantaneous nucleation at the start of the reaction may be assumed (the first version). This means that in a crystal there exist from the beginning a number of points—nuclei connected with the regions of the disordered structure of physical nature, i.e., as has been mentioned above, dislocations escaped to the surface, vacancies, accumulations of ions in the interstices, the sites of adjoining of the sharp edges of the crystal faces, etc. In other words, the invariable initial number of nuclei  $N_0$  is assumed here. In this case, the kinetic law must be determined by the shape of the nuclei produced and by the rate of their growth. If we as-

sume, in a simple version, the formation of spherical nuclei and the constant rate,  $K_g$  in cm/sec, of their radial growth, then the radius of the nucleus will be  $K_gt$  and the volume of all the nuclei, i.e., the amount of substance reacted in the initial state of the reaction when the nuclei do not overlap, is expressed by the relation

$$\frac{4}{3} \pi N_0 K_g^3 t^3 \tag{13.2}$$

Thus, in this case there is obtained the cubic relation  $\alpha = f(t)$ , which does not, on the whole, satisfy the experimental data.

Another law of nucleation is the assumption of the first kinetic order of the rate of their appearance (the second version). In this case, it is supposed that the substance contains a number of particular points which are less chemically stable than the remainder mass of the crystal. These are not yet nuclei but they grow into nuclei by way of some activation process. If the stability of the substance at all the points is the same, then the probability of activation of each point may be set equal to

$$v_{\rm exp}\left(-\frac{\Delta G^{\neq}}{RT}\right) \tag{13.3}$$

where v is some frequency factor and  $\Delta G^{\neq}$  is the energy of activation (Gibbs). The rate of nucleation will then be proportional to the number of points that have not yet been activated by the time considered. If at time zero there are altogether  $N_0$  points capable of being activated and the potential centres are not yet captured by the product, then the number of nuclei by time t will be determined by the following first-order equation:

$$N_t = N_0 \left( 1 - e^{-kt} \right) \tag{13.4}$$

where k is the rate constant for nucleation. At small t the function (13.4) may be expanded into a series and only the first term left. This will give the number of nuclei formed by time t, which is proportional to time, i.e.,

$$N_t = N_0 kt$$

Using the last expression in combination with formula (13.2) obtained on the assumption of the constant radial rate of formation of spherical nuclei, we find that  $\alpha \sim t^4$  for the initial step of decomposition.

We should also consider the law of nucleation at an increasing rate (the third version).

We shall discuss here the method proposed by Bagdasaryan in 1945. During the formation of a growing nucleus there must occur β consecutive elementary processes, the probability of which

is the same and equal to  $k_1$ . In essence, in this model it is assumed that if all  $N_0$  nuclei have the same size at t=0, then the number of actively growing nuclei at time t is equal to the number of nuclei, each of which has successively added p atoms of the product. After some time there will be observed the following size distribution of the nuclei:

 $n_0$  remain to be nuclei  $n_1$  have added 1 atom of product  $n_2$  have added 2 atoms of product  $n_i$  have added i atoms of product

Let us examine the change of this distribution with time. In a general form, assuming the occurrence of a first-order reaction, we may write the rate of change of the number of growing nuclei:

$$\frac{dn_j}{dt} = k_{j-1}n_{j-1} - k_j n_j \tag{13.5}$$

where  $k_j n_j$  is the number of atoms that add on to the nuclei of the j class per unit time, as a result of which they turn into the j+1 class. Accordingly,  $k_{j-1}n_{j-1}$  is the rate of formation of nuclei of the j class from the j-1 nuclei.

In a more detailed treatment we may first write

$$\frac{dn_0}{dt} = -k_0 n_0$$

$$\frac{dn_1}{dt} = k_0 n_0 - k_1 n_1$$

$$\frac{dn_2}{dt} = k_1 n_1 - k_2 n_2$$

$$\frac{dn_i}{dt} = k_{i-1} n_{i-1} - k_i n_i$$
(13.6)

In solving these equations we must take into account the following boundary conditions: all  $n_i$ , except for  $n_0$ , are equal to zero at  $t \to \infty$ , and  $n_0$  is equal to zero at  $t \to \infty$ .

To solve this system of equations it is also necessary to know the dependence of  $k_i$  on i, i.e., on the number of steps that have been accomplished. This dependence is unknown. Therefore, an approximation is used here, assuming first that

$$k_0 = k_1 = k_2 = \dots = k_{n-1} = k_1$$

and, second, that

$$k_p = k_{p+1} = k_{p+2} = K$$

K being the rate constant for a growing nucleus; it is much greater than the constant k which refers to the induction period. Namely, according to Bagdasaryan,

$$K = ke^{\Delta \varepsilon / RT}$$

in which expression  $\Delta \varepsilon$  is an additional quantity of activation energy characteristic of the induction period.

Integrating the first two equations of the system (13.6), we obtain

$$n_1 = k_1 N_0 t e^{-k_1 t} (13.7)$$

Then, we write the following relation

$$\frac{dn_2}{dt} = k_1 n_1 - k_1 n_2 = k_1^2 N_0 t e^{-k_1 t} - k_1 n_2 \tag{13.8}$$

where Eq. (13.7) is taken into account. Integrating Eq. (13.8) in the usual manner, we find

$$n_2 = N_0 \frac{(k_1 l)^2}{2!} e^{-k_1 l}$$
 (13.9)

or, in general,

$$n_i = N_0 \frac{(k_1 t)^i}{i!} e^{-k_1 t}$$

The number of all actively growing nuclei, n, formed during the time t, is found by summing up all  $n_i$  at i ranging from p to  $\infty$ , i.e.,

$$n = N_0 e^{-kt} \sum_{p}^{\infty} \frac{(k_l t)^4}{i!}$$
 (13.10)

This expression may now be represented in a somewhat different form. Since

$$e^{kt} = \sum_{0}^{\infty} \frac{(kt)^{i}}{i!} = \sum_{0}^{p-1} \frac{(kt)^{i}}{i!} + \sum_{0}^{\infty} \frac{(kt)^{i}}{i!}$$

then it follows that

$$n = N_0 \left[ 1 - e^{-kt} \sum_{i=0}^{p-1} \frac{(kt)^i}{i!} \right]$$
 (13.11)

These equations are however employed in simplified form specifically for the solution of the problems of the kinetics of topochemical reactions. Thus, certain considerations lead to the conclusion that for the initial period of time the quantity kt is always essentially less than unity, and therefore Eq. (13.10) may be represented in the following simple form

$$n = N_0 \frac{(kt)^p}{p!} \tag{13.12}$$

which expresses the power dependence of the number of actively

growing nuclei on time.

The next step in the calculation of the kinetics of a topochemical reaction may consist in the following. Having chosen, on the basis of some more or less substantiated data, the law of nucleation, we should make assumptions as to the shape of the nuclei being formed and the laws of their growth. All this makes it possible to derive a kinetic equation in the form, say, of the dependence  $\alpha = f(t)$ .

We have considered here only the method worked out by the Soviet school: Kolmogorov, Erofeev, and Bel'kevich. The well-known Erofeev formula

$$\alpha = 1 - e^{-kt^n} \tag{13.13}$$

is based on the works of Kolmogorov, who studied the process of crystallization. Kolmogorov has derived two equations describing the conversions in the crystallizing system resulting from (a) the growth of a constant number of spherical nuclei with account taken of their overlap; (b) the growth of spherical nuclei, the number of which increases at a constant rate, also with account taken of the overlap of nuclei.

Let us first consider the first variant. During the entire course of the reaction there are  $n_0$  nuclei per unit volume and the fraction of the substance reacted by time t is given by the expression

$$\alpha = \frac{4}{3} \pi n_0 K_g^3 t^3 \tag{13.14}$$

where  $K_g$  is the rate of the radial growth of a spherical nucleus. The rate of the reaction at this time is expressed by the derivative

$$\frac{d\alpha}{dt} = 4\pi n_0 K_g^3 t^2 = K_g \left[ 4\pi n_0 K_g^2 t^2 \right]$$

In other words, the reaction rate is proportional to the total surface area of the nuclei. However, because of the overlap of nuclei, the actual interface, on which the crystallization takes place or the reaction proceeds and to which the reaction rate is proportional, is less than the sum of the surface areas of the separate nuclei. For a random distribution of nuclei it may be assumed that the fraction of the effective surface area is equal to  $(1-\alpha)$  of the total surface area. Thus, the reaction rate, with account taken of the overlap of nuclei, is equal to

$$\frac{d\alpha}{dt} = 4\pi n_0 K_g^3 t^2 (1 - \alpha)$$

Or, integrating, we obtain

$$\alpha = 1 - e^{-\frac{4}{5}\pi n_0 K_g^3 t^3} = 1 - e^{-kt^2}$$
 (13.15)

where the reaction time raised to the third power appears in the exponent.

In the second variant the rate of nucleation is assumed to be constant. This may also occur in the case of the earlier considered first and a law when a second first a law wh

first-order law when  $n_t = n_0 kt$  for the initial stage.

In this case, the number of nuclei formed during the time interval from  $t = \tau$  to  $t = \tau + d\tau$  is equal to  $dn = kn_0 d\tau$ , and the volume of these nuclei by time t will be

$$d\alpha = \frac{4}{3} \pi k n_{\rm G} K_{\rm g}^{3} (t - \tau)^{3} d\tau$$

Integrating this expression from  $\tau = 0$  to  $\tau = t$ , we find the volume of all nuclei by time t:

$$\alpha = \frac{1}{3} \pi k n_0 K_g^3 t^4$$

The reaction rate at this time will be written thus:

$$\frac{d\alpha}{dt} = \frac{4}{3} \pi k N_0 K_g^3 t^3$$

Then, the overlap of nuclei is again taken into account:

$$\frac{d\alpha}{dt} = \frac{4}{3} \pi k n_0 K_g^3 t^3 (1 - \alpha)$$

whence

$$\alpha = 1 - e^{-\frac{1}{4\pi} \pi k n_0 K_g^3 t^4}$$

or

$$\alpha = 1 - e^{-kt^{1}} \tag{13.16}$$

Here the reaction time in the exponential function is found to be raised to the fourth power. The Erofeev equation is a generalized form of Eqs. (13.15) and (13.16). It can be derived by using the law of nucleation at an increasing rate, the law deduced by Bagdasaryan. It is assumed here that for the conversion of any one of the  $n_0$  nuclei into an actively growing nucleus there are required  $\sigma$  consecutive steps with the rate constants  $k_1, k_2, \ldots, k_{\sigma}$ . Omitting the derivation, we write directly the Erofeev equation:

$$\alpha = 1 - e^{-\frac{8\pi n_0 k_1 k_2 \dots k_{cr}}{(\sigma + 3)!} K_g^3 t^{\sigma + 3}}$$

or

$$\alpha = 1 - e^{-kt^n} \tag{13.17}$$

where  $n = \sigma + 3$  and  $\sigma$  has the meaning of the number of elementary steps in the transformation of a nucleus to an actively

growing nucleus. In a more complete treatment the exponent n is expressed by the sum

$$n = a + \sigma \tag{13.18}$$

where  $\sigma$  is the number of steps and a depends on the number of directions in which the nuclei grow. Thus, a=1 if the nuclei grow in one direction, a=2 for two directions and a=3 for three directions.

The constants k and n entering into Eq. (13.17) are found by the treatment of experimental data, using the relation

$$\ln\left[-\ln\left(1-\alpha\right)\right] = \ln k + n \ln t \tag{13.19}$$

Consequently, the double logarithm of  $1/(1-\alpha)$  must be a linear function of the time logarithm. It is however better to make use of the following relation in order to find n:

$$\left[\log \frac{1}{1-\alpha}\right]^{1/n} = k^{1/n}t \tag{13.20}$$

Let us also consider the concept of the chain nature of topochemical reactions proposed by Garner (1933). According to Garner, the reaction begins on  $N_0$  centres, the activation of which occurs at a constant rate. During the decomposition there is developed a thin filament of the product, which is growing until it encounters one of the cracks in the crystal lattice, this involving the formation of new filaments, which in their turn grow and develop. If we ignore the overlap of nuclei, which does not play an important part in the early stage of the reaction, then the overall rate of nucleation will be given by

$$\frac{dN}{dt} = k_0 N_0 + k_b N \tag{13.21}$$

where  $k_0$  is the rate constant for the activation of the initial centres, and  $k_b$  characterizes the probability of branching.

The Garner model has been refined by Prout and Tompkins who proposed taking account of the overlap of linear chains when the decomposition has gone too far. In view of this, an additional term, which takes into account the probability of chain termination, this being proportional to N, i.e., to the number of nuclei at time t, was introduced into the Garner equation (13.21). Thus, using the notations of the authors, we obtain

$$\frac{dN}{dt} = k_1 N_0 + k_3 N - k_4 N \tag{13.22}$$

where  $k_1$  is the rate constant for the activation of centres,  $k_3$  is the probability of branching, and  $k_4$  is the probability of chain termination. If the rate constant of nucleation,  $k_1$ , is large, then the initial potential centres are rapidly consumed, in which case we

may use the simplified equation

$$\frac{dN}{dt} = (k_3 - k_4) N ag{13.23}$$

All the same, even if  $k_1$  is small, the branching process must predominate and  $(k_3 - k_4)N \gg k_1N$ . In any event, it is assumed that

$$\frac{d\alpha}{dt} = k'N \tag{13.24}$$

This expression considered to be also valid for strictly linear nuclei. Equations (13.23) and (13.24) are the basic equations in the Prout-Tompkins theory. Further, for the purpose of integration it is necessary to assume a functional relation between the extent of reaction  $\alpha$  and the probabilities  $k_3$  and  $k_4$ . The authors consider a special case of a symmetrical sigmoid curve (see Fig. 13.1), the inflection point of which corresponds to  $\alpha_i = \frac{1}{2}$ . At the start of the reaction  $(t = 0, \alpha = 0) k_4$  is also equal to zero since at this stage no interception is possible. At the point of inflection, at  $\alpha = \alpha_i$ , dw/dt changes its sign and hence  $k_3 = k_4$  at  $\alpha = \frac{1}{2}$ . Therefore, it seems to be reasonable to apply the following relation

$$k_1 = \frac{\alpha}{\alpha_i} k_3 \tag{13.25}$$

The probability  $k_3$  depends on the geometry of the crystal lattice, but for a given substance it is constant. Thus, from Eqs. (13.23) and (13.24) we obtain

$$\frac{dN}{dt} = k_3 \left( 1 - \frac{\alpha}{\alpha_I} \right) N = \frac{k_3}{k'} \left( 1 - \frac{\alpha}{\alpha_I} \right) \frac{d\alpha}{dt}$$
 (13.26)

or

$$\frac{dN}{dt} = \frac{k_3}{k'} \left( 1 - \frac{\alpha}{\alpha_I} \right)$$

and also, separating the variables,

$$dN = \frac{k_3}{k'} \left( d\alpha - \frac{1}{\alpha_i} \alpha \, d\alpha \right)$$

Integrating, we get

$$N = \frac{k_3}{k'} \left( \alpha - \frac{\alpha^2}{2\alpha_i} \right) \tag{13.27}$$

This expression for N is substituted into Eq. (13.24) and at  $\alpha_i = 1/2$  the following relation obtains:

$$\frac{d\alpha}{dt} = k_3 (1 - \alpha) \alpha \tag{13.28}$$

which is a differential form of the Prout-Tompkins equation. It evidently coincides with the term of the Ostwald equation (12.40),

which expresses the autocatalytic acceleration of the reaction. Integration of Eq. (13.28) by decomposing the fraction into partial fractions gives the well-known integrated form of the Prout-Tompkins equation:

$$\ln \frac{\alpha}{1-\alpha} = k_3 t + C \tag{13.29}$$

which is also employed in the analysis of experimental data.

It should be noted that at the present level of development of the kinetics of topochemical reactions it is often found to be difficult to decide what model and, hence, what equation, must be given preference in the discussion of experimental data.

## 13.3. Some Experimental Data on Kinetics of Decomposition of Solids

Let us now consider some concrete reactions and, in the first place, the thermal decomposition of potassium permanganate, which has been extensively investigated in the works of the Soviet school of kineticists; the reaction proceeds evidently by the stoichiometric equation

$$2KMnO_4 \longrightarrow K_2MnO_4 + MnO_2 + O_2$$

The effect of various factors on the kinetics of this reaction has been studied by Erofeev. For example, he studied the role of purification of the starting material by recrystallization. The reaction was conducted in the closed volume of the vacuum apparatus, the pressure of the oxygen formed being measured.

Figure 13.3 is a typical sigmoid curve showing the time dependence of the oxygen pressure in experiments with the unrecrystallized starting permanganate. In the kinetic calculations use was made of Eq. (13.17); on the basis of Eq. (13.19) there were plotted graphs of  $\log [-\log (1-\alpha)]$  versus the logarithm of the reaction time. Examples of such plots for a series of experiments conducted at a single temperature are presented in Fig. 13.4. As seen from this figure, there is really obtained a straight-line dependence for a considerable part of the reaction time but at the end of the reaction there is observed an upward curvature of the experimental curve, which is formally described by the increase of the exponent t; but, in essence, it may be associated with the crudeness of the assumption of the proportional relation between the probability of nucleation and the amount of substance reacted. Table 13.1 lists the values of n and  $\log k$  calculated from the equation  $\log [-\log (1-\alpha)] = n \log t + \log k$ .

Thus, the value of the coefficient n is close to the integer 2. This may be interpreted as an indication that the faces of the crystals of the unrecrystallized starting permanganate are covered

by a layer of the decomposition products, as a result of which they are potential centres. This is consistent with the fact of the visible absence of localized reaction nuclei when observed under the microscope. To put it in a different manner, the formation of flat

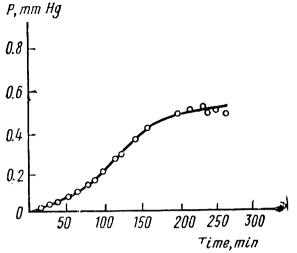


Fig. 13.3. A typical pressuretime curve for the decomposition of unrecrystallized potassium permanganate at 218 °C (after Erofeev and Smirnova).

Fig. 13.4. The dependence of  $log [-log (1-\alpha)]$  versus log t for the decomposition of unrecrystallized potassium permanganate at 218 °C.

The curves are shifted to the right by 0.3 for experiment 4; by 0.5 for experiment 3; and for experiment 2 they are shifted to the left by 0.2 scale units.

decomposition surfaces proceeds in a single stage ( $\sigma = 1$ ) and the decomposition itself proceeds in the direction perpendicular to the plane of the face (a = 1); thus,  $n = a + \sigma = 2$  [see Eq. (13.18)].

TABLE 13.1. The Constants n and log k of Equation (13.17) for Experiments on the Kinetics of the Decomposition of the Unrecrystallized Potassium Permanganate at 218 °C

KMnO <sub>4</sub> , mg	n	log k	Upper limit of applicability of Eq. (13.17) α, %	Remarks
34.8	1.84	-8.26	86	Preliminary degas-
43.9	1.89	-8.18	60	sing at 100°C
34.8	1.85	-8.28	56	Preliminary degas-
34.3	2.12	-8.22	82	sing at 100°C

Figure 13.5 shows a curve calculated at n=2 and  $\log k=-8.26$  (experiment 1, Fig. 13.4) and the experimental points.

On the whole, it is seen that the calculated curve agrees satisfactorily with the experimental data.

In another work Erofeev investigated, using the same procedure, the kinetics of the thermal decomposition of potassium permanganate purified by recrystallization. Two series of experiments

were carried out: the decomposition of the permanganate in the form of crystals, produced directly by recrystallization, thoroughly ground crys-The decomposition was conducted at temperature ranging from to 227 °C. For the dependence  $\alpha = f(t)$  there have been obtained typical sigmoid curves of autocatalytic nature, which are similar to those shown in Figs. 13.1 and 13.3. From the oxygen pressure there was calculated the average reaction rate

$$w = \frac{\Delta \alpha}{\Delta t} = \frac{1}{P_{\infty}} \cdot \frac{\Delta P}{\Delta t}$$

An example of the dependence of the reaction rate

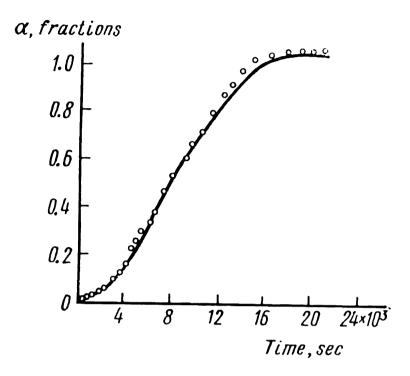


Fig. 13.5. The kinetics of the thermal decomposition of unrecrystallized potassium permanganate at 218°C.

The circles are the experimental data; the curve has been calculated by the equation  $\alpha = 1 - \exp \{-|\exp (-19.02)| t^2\}$ .

on the reaction time is given in Fig. 13.6. We can clearly see the induction period and the maximum of the reaction rate attained

TABLE 13.2. The Kinetic Characteristics of the Reaction of Decomposition of Recrystallized Potassium Permanganate

t, °C	n, integer	log k	Limits of applicability of Eq. (1:	
			a <sub>lower</sub> . %	a <sub>upper</sub> , %
	Unground	d sample		
211.5	4	-16.346	7.1	93.7
217	5	-17.816	5.3	90.4
	Ground	sample		
211.5	4	-16.133	13.4	98.8
227.5	4	-14.180	15.7	95.9

almost exactly at  $\alpha_m = 0.5$ . Grinding of the permanganate did not result in any significant change of the kinetics of its decomposition but still led to a somewhat energetic self-acceleration of the reaction and to somewhat higher values of  $\alpha_m$ .

Figure 13.7 shows the plots of  $\log[-\log(1-\alpha)]$  versus  $\log t$  obtained in this series of experiments. From this figure it is seen that the straight-line character of the graph, which is characteristic of a considerable part of the intermediate step of the reaction (Table 13.2), is disturbed at the initial and final

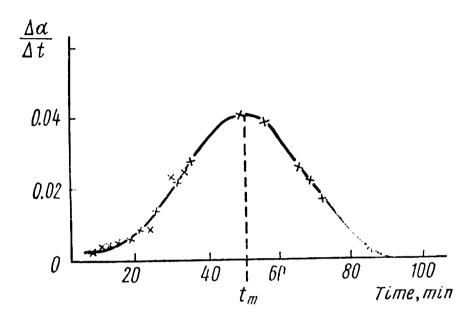


Fig. 13.6. The dependence of the rate of decomposition of unrecrystallized unground potassium permanganate on time. The temperature is 227 °C. To the maximum there correspond:  $\alpha_m = 0.508$ ;  $t_m = 50.4$  min.  $(\Delta \alpha/\Delta t)_m = 0.0416$  min<sup>-1</sup>.

stages. Perhaps, a second straight line should have been plotted and considered separately for the initial step.

In the work under discussion the exponent n was calculated by two methods. First, as before, from the straight lines of Fig. 13.7 and, second, from the maximal reaction rate (Fig. 13.6) in accordance with the relation

$$n = 1 + \frac{(\Delta \alpha / \Delta t)_m t_m}{1 - \alpha_m}$$

The value of k was calculated by the formula

$$\log k = \log \left[ -\log \left( 1 - \alpha \right) \right] - n \log t$$

Here an integral value closest to the experimental value (Table 13.2) was assumed for n in this calculation.

According to Erofeev\*, in the case where the reaction nuclei grow from separate points on the surface of the crystal in three

<sup>\*</sup> Erofeev, B. V., Izv. Akad. Nauk BSSR, 4, 137 (1950).

directions,  $n = \sigma + 3$ , where, as is already known,  $\sigma$  is the number of consecutive steps in the process of formation of the product nuclei. Thus, the value of n = 4 in the case of the finely divided compound indicates that the nucleation proceeds in one stage. On the other hand, for the unground sample of  $KMnO_4$  the value of n was equal to 5 in most of the experiments, which corresponds to two consecutive steps in the formation of initial decomposition centres. Besides, it was noted that n increases from 4

to 5 with rise of temperature from 211-216 to 227 °C for

the unground sample.

All these findings been explained in the following manner. It is possible that at lower temperatures even one molecule of the solid product is an initial centre of nuclear growth. At higher temperatures the initial centre consisting of one molecule of the solid product is unstable and the catalytic process becomes possible only when an initial centre is formed from two molecules of the solid product (n = 5). It is also possible that when the permanganate is finely divided (when in all the cases

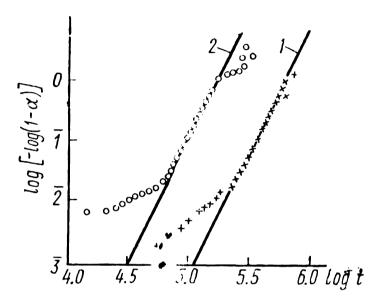


Fig. 13.7. The dependence of  $\log [-\log (1-\alpha)]$  on  $\log t$  (time in seconds) for the decomposition of recrystallized potassium permanganate at 227 °C (curve 1) and 222 °C (curve 2). The unground sample. The curves 1 and 2 are shifted to the left along the abscissa by 2.1 and 1.7 scale units, respectively.

n=4), on the newly formed crystal surface there appear such irregularities (defects) on which the initial centres consisting of one product molecule are stable at all the temperatures studied. The values of the exponent n=4 and n=5 point to the growth of three-dimensional product nuclei (say, spherical, see Fig. 13.2). Herein lies the essential difference between the kinetics of the decomposition of recrystallized and unrecrystallized KMnO<sub>4</sub>, the value of n for the latter being equal to 2, which, as has already been said, is an indication that the reaction is triggered simultaneously over the entire surface of the crystal faces.

A comparison of the data for the ground and unground samples shows the absence of a substantial effect of the grinding operation on the general trend of the kinetics of the reaction. From this we may conclude that the self-crushing of the crystals during the reaction and the associated increase of their surface area are not the main factors responsible for the self-acceleration of the reaction.

It should be noted further that, in spite of the departure from the straight-line dependence (Fig. 13.7), the constants found on the basis of these straight lines enable one to describe, to a rather good approximation, the course of the integral decomposition curve  $\alpha = f(t)$ . As an example may be cited the comparison of the curve with the experimental points (Fig. 13.8).

We shall present some data on the kinetics of the thermal decomposition of other solids. For example, in still another work

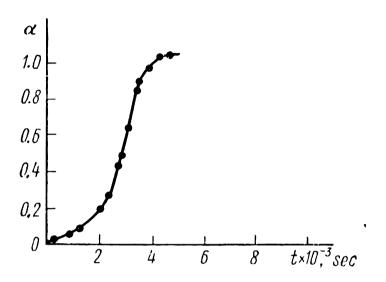


Fig. 13.8. The solid curve has been calculated by the equation  $\alpha = 1 - \exp \times (-3.52 \times 10^{-18} t^5)$ .

The points are the experimental data for recrystallized unground potassium permanganate at  $227\ ^{\circ}\text{C}.$ 

Erofeev studied the kinetics of the thermal decomposition of manganese formate

$$Mn(HCOO)_2 \longrightarrow$$
 $\longrightarrow Mn + CO + CO_2 + H_2O$ 
and of lead formate

$$\begin{array}{ccc} 2\text{Pb}(\text{HCOO})_2 & \longrightarrow \\ & \longrightarrow & 2\text{Pb} + 3\text{CO}_2 + \text{CH}_2\text{O} + \text{H}_2 \end{array}$$

It has been established that the experimental data are described by Eq. (13.17) at n = 2. As known, this corresponds first to a single-stage nucleation process and, second, to the growth of nuclei in one direction.

According to Erofeev, the first case may occur if the formation of initial centres in the decomposition of the formates is a process of formation of metal atoms as a result of the reaction taking place on the surface:

$$Me(HCOO)_2 \longrightarrow Me + H_2 + 2CO_2$$

The adsorbed  $H_2$  and  $CO_2$  molecules are then removed into the gas phase.

In this case, the rate of formation of initial centres is a first-order process:

$$\frac{d |Me|}{dt} = k_{\infty} [Me(HCOO)_2]_{surface} = k\gamma_0 e^{-k_0 \tau}$$

where  $\gamma_0 = [Me(HCOO)_2]$  is the surface concentration of the formate molecules, and  $\tau$  is the time. The growth of nuclei in one direction means that the decomposition reaction spreads very rapidly over the entire surface area of the crystal, as a result of which the faces of the crystals are covered by a metal layer. It is for this reason that the subsequent decomposition reaction proceeds only in a single direction perpendicular to each of the faces.

On the basis of these considerations there is derived the following equation:

$$\alpha = 1 - \exp\left[-\frac{N_0 M S_0 \gamma_0 k_0}{2} t^2\right] = 1 - e^{-kt^2}$$

where  $N_0$  is the number of crystals in the weighed amount, M is the number of faces in the crystals,  $S_0$  is the average size of the faces,  $\gamma_0$  is the surface concentration of formate molecules, and  $k_0$  is a constant.

From the foregoing it is clear that the kinetics of the decomposition of solids depend on many factors and, in particular, on the history of the samples being studied. Thus, many authors have noted the effect of the "aging" of the samples on the kinetics of decomposition: freshly prepared samples decomposed differently from those kept for some time. Table 13.3 lists the results of the investigations carried out by Boldyrev \*, who studied the effect of the aging time on the kinetics of the decomposition of lead oxalate (Pb $C_2O_4$ ) at 336 °C.

TABLE 13.3. The Kinetic Characteristics of the Thermal Decomposition of Lead Oxalate Aged at 120 °C

Aging time, hr	K, min <sup>-1</sup>	n
2	0.130	1.96
4	0.100	2.16
8	0.048	2.40
14	0.015	2.80

From Table 13.3 it is seen that the exponent n in Eq. (13.17) increases under the influence of aging from about 2 to about 3, which is probably associated with some processes occurring on the crystal surface.

Table 13.3 gives another quantity, K, instead of the constant k of Eq. (13.17); K has the dimensions of the inverse time; it is related to k by the relation proposed by Sakovich \*\*:

$$K = nk^{1/n} \tag{13.30}$$

According to the data of Table 13.3, the rate constant K falls off with increasing duration of aging. As the temperature mounts the value of n also increases and K decreases. But no much emphasis should be placed on the latter circumstance since the

<sup>\*</sup> Boldyrev, V. V., The Effect of Defects in Crystals on the Rate of Thermal Decomposition of Solids, Tomsk, Izd. TGU, 1963, pp. 114-145 (in Russian).

\*\* Sakovich G. V., Uchen. Zapiski Tomskogo Universiteta, 26, 103 (1955).

recalculation of the constant by means of Eq. (13.30) is more formal. Relation (13.30) is based on the following considerations. Differentiating Eq. (13.17), we can write the reaction rate in the form

$$w = \frac{d\alpha}{dt} = nk^{1/n} (1 - \alpha) [-\ln (1 - \alpha)]^{(n-1)/n}$$
 (13.31)

which has the meaning of the rate law and is reminiscent of the law of mass action. The coefficient before the terms containing  $\alpha$ , i.e.,  $nk^{1/n} = K$ , may be called the rate constant.

In a number of works, in this connection the values of k experimentally found from Eq. (13.17) are used to calculate [relation (13.30)] the constant K, which apparently exhibits better constancy. The following reasoning is in favour of this. The coefficient n may vary for the same reaction because of many factors—with change of temperature (Table 13.2), purity of the sample, and, in general, its history (Table 13.3), but this is evidently as-

TABLE 13.4. Thermal Decomposition of Nickel Oxalate with Lithium and Scandium Added

	Average value of n at temperature, °C		
Substance added	280	290	300
No substance added	3.60	3.30	3.80
Lithium	4.18	4.16	4.10
Scandium	2.93	2.69	2.75

sociated also with the change of the dimensions of k equal to  $[t^{-n}]$ . Besides, as pointed out by Sakovich, the activation energies calculated from the temperature dependence of K are closer to those determined by other methods than the activation energies found from the values of k.

As has already been pointed out, the initial decomposition centres are probably the defects of the crystal lattice. Interesting in this connection are the attempts to produce defects artificially. Thus, Erofeev and Mostovaya have studied the decomposition of nickel oxalate with added substances of a different valency, namely, lithium as a metal of lower valency (0.145-6.0 mol. %) and scandium as a metal of higher valency (0.13-3.05 mol. %). The results obtained are presented in Table 13.4.

Thus, the lithium added increases n, and scandium decreases it. These changes are ascribed by the authors to the increase of positive holes in the crystal lattice of nickel oxalate to which lithium is added and also to their decrease in the samples doped

with scandium. It is believed that in the presence of positive holes the formation of initial growth centres of the solid product nuclei is possible only after their destruction as a result of the recombination with the electrons supplied by thermally decomposing anions. Associated with this is the increase of the number of electrons consumed, on an average, for the formation of initial centres and the corresponding increase of the exponent n when lithium is added.

On the other hand, in samples doped with scandium, part of the nickel atoms may be in the state Ni<sup>+</sup> or Ni<sup>0</sup> so that for the initial growth centres of the nuclei of the solid product to be formed on them, a smaller number of electrons is required, which is what reveals itself in the decrease of the parameter n. Thus, the variation of n is the result of the change, under the influence of the added substances, of the number of elementary steps in the process of formation of initial centres of the decomposition of nickel oxalate.

The study of the kinetics of topochemical reactions is a rather complicated task, which is accounted for, say, by the difficulty of creating isothermal conditions for the reaction, especially in the early stages. Furthermore, there are too many factors which exert an influence on the reaction velocity and which make it difficult to obtain reproducible results. It often happens that the experimental curve is more or less satisfactorily described by various kinetic equations. Since each of them is associated with various models, it is very difficult to decide which model should be used and to draw an unambiguous conclusion as to the mechanism of the reaction. As an example, reference may be made to the work of Prodan and Pavlyuchenko\* on the thermal decomposition of cadmium carbonate in vacuum. The authors refer, first, to the literature data, according to which the rate of the decomposition of cadmium carbonate, depending on time, may pass through a maximum or be the largest from the start of the reaction and described by various equations:

1. 
$$\frac{d\alpha}{dt} = k\alpha^{4/3}(1-\alpha) \quad 2. \quad 1-\sqrt[3]{1-\alpha} = kt/3$$

$$3 \quad \frac{d\alpha}{dt} = k\alpha^{2/4} \qquad \qquad 4. \quad \frac{d\alpha}{dt} = k \left(1 - \alpha\right)^{1/2}$$

5. 
$$\alpha = 1 - e^{-kt^n}$$
 6.  $\log \frac{1}{1 - \alpha} = kt/2.5$ 

7. 
$$\ln \alpha = kt + C$$
 8.  $\ln \frac{\alpha}{1 - \alpha} = kt + C$ 

<sup>\*</sup> Heterogeneous Chemical Reactions. Edited by M. M. Pavlyuchenko, Minsk, Izd. MV SSO, 1961, p. 79 (in Russian).

Second, on the basis of the experimental data obtained by these authors, they come to the conclusion that the kinetics of the thermal decomposition of cadmium carbonate are satisfactorily described by Eqs. (5), (2), and (6), and that the rate constants and activation energies calculated with the aid of these equations have close values.

And yet, judging by a set of numerous data, the Erofeev-Kolmogorov equation more frequently describes satisfactorily the kinetics of topochemical reactions at the various decomposition stages. It is for this reason that much attention has been paid here to this equation.

# CHAPTER 14

# Kinetics of Chemical Reactions in the Thermodynamics of Non-Equilibrium Processes

We shall here consider briefly the application of methods used in the thermodynamics of non-equilibrium (irreversible) processes to chemical reactions. As is known, the ordinary formula of the second law of thermodynamics has the form

$$dS \equiv \delta Q/T \tag{14.1}$$

where S is the entropy of the system,  $\delta Q$  is the heat absorbed by the system, and T is the temperature. The equality sign refers to equilibrium processes, which constitute the only subject studied in the courses of ordinary thermodynamics. The "greater than" sign characterizes a spontaneous non-equilibrium process and is commonly used only as a criterion of the direction of spontaneous processes. For the case of inequality Clausius proposed a different manner of writing the second law, using the relation

$$dS - \delta Q/T \equiv \delta Q'/T \tag{14.2}$$

to define a certain quantity  $\delta Q'$  called the **uncompensated heat** by Clausius. It should be admitted that this term is not quite adequate since this is not the heat actually absorbed or evolved by the system but the heat that would have been absorbed in an equilibrium process in addition to the non-equilibrium amount  $\delta Q$  in order to restore the equilibrium (14.1). On the basis of Eq. (14.2) we can write the second law in the following most general form:

$$dS = \delta Q/T + \delta Q'/T \tag{14.3}$$

From these relations it must be clear that for equilibrium processes  $\delta Q'=0$ , and for non-equilibrium processes

$$\delta Q' > 0 \tag{14.4}$$

In other words,  $\delta Q'$  is always positive and appears as if inside the system as a result of non-equilibrium processes leading to its irreversible change.

The physical significance of the uncompensated heat  $\delta Q'$  will become clearer if the total change of the entropy of the system is split into two components:

$$dS = d_e S + d_i S \tag{14.5}$$

where  $d_eS$ , the external change of the entropy, is associated with the equilibrium absorption of heat from outside, and  $d_iS$  is the internal change of the entropy caused by non-equilibrium processes taking place inside the system. Comparing Eqs. (14.3) and (14.5), we may write:

$$d_e S = \delta Q/T \tag{14.6}$$

$$d_i S = \delta Q'/T \tag{14.7}$$

The last relation connects the uncompensated heat with the so-called entropy appearance  $(d_iS)$  in the system due to the non-equilibrium processes occurring in it.

Relations (14.4) and (14.7) should be understood in the sense that any non-equilibrium process in the system (for example, the mixing of gases, spontaneous release of the compressed spring, etc.) increases the randomness, or disorder, of the molecular state of the system, leading to a greater chaos or "mixtupness" of the system. A quantitative manifestation of this increased disorder is the increase of the thermodynamic probability of the state of the system and, hence, the increase of the entropy of the system. Thus, the uncompensated heat, which is the basic quantity in non-equilibrium (or irreversible) thermodynamics, is equal, according to Eq. (14.7), to the appearance of entropy multiplied by temperature  $(Td_iS)$ .

Non-equilibrium processes, in contrast to equilibrium processes, proceed at a finite rate; their study is essentially within the scope of kinetics, both physical and chemical. Therefore, in considering such processes we introduce the time, a parameter that is completely left out in ordinary equilibrium thermodynamics. Thus, if the entropy  $d_iS$  arises during the time dt, then we speak of the rate of appearance of entropy:

$$\sigma = d_i S/dt \geqslant 0 \tag{14.8}$$

It is exactly the values of  $\sigma$  that we are going to calculate now. For an isolated system (U = constant, V = constant) the total change of the entropy of the system is equal to the internal entropy change, i.e.,

$$dS_{U,V} = d_i S \geqslant 0 \tag{1.4}$$

On the basis of the combined formula of the first and second laws of thermodynamics

$$\delta Q = dU + p \, dV = T \, dS - \delta Q \tag{1-.1}$$

it is easy to show the relation between  $\delta Q'$  and, hence,  $d_i S$ , and the changes of other thermodynamic functions. Namely,  $\delta Q' = T d_i S = -dU_{S,\,V} = -dH_{S,\,P} = -dF_{T,\,V} = -dG_{T,\,P}$ , where the subscripts  $S,\,V;\,S,\,P$ , etc., signify the constancy of data on the given thermodynamic properties of the system.

Turning to the kinetics proper, we write the equation of a hypo-

thetical general chemical reaction in a general form:

$$v_1 B_1 + v_2 B_2 + \dots = v_1' B_1' + v_2' B_2' + \dots$$
 (14.11)

where  $v_i$ s are stoichiometric coefficients, and  $B_i$ s are the symbols for the substances—the participants of the reaction. Suppose that the reaction proceeded from left to right, so that the number of moles of substances  $B_i$  changed by  $dn_i$ . Let us determine the change of the chemical variable  $\xi$  with the aid of the relation

$$d\xi = dn_i/v_i \tag{14.12}$$

indicating the "completeness" of the occurrence of the reaction. If  $\Delta \xi = 1$ , the reaction is said "to have accomplished one run". In 1922 de Donder introduced the following definition of chemical affinity A in terms of the Clausius uncompensated heat:

$$\delta Q' = A \, d\xi \geqslant 0 \tag{14.13}$$

As before, the equality sign corresponds to equilibrium, and the "greater than" sign corresponds to the spontaneous, i.e., non-equilibrium, course of the reaction. As a whole, relation (14.13) is called the de Donder inequality. It can however be shown that the definition (14.13) is not so much different from the classical definitions of chemical affinity. Thus, using relation (14.11) and also the definition of the standard chemical potential of a substance  $\gamma$  of a mixture according to Gibbs,  $\mu_{\gamma} = (dG/bn_{\gamma})_{P,T,v_{\gamma}}$ , we can write the following relation

$$A = -\left(\partial G/\partial \xi\right)_{T, P} = -\sum \left(v_{\gamma} \mu_{\gamma}\right) \tag{14.14}$$

Van't Hoff and Helmholtz had earlier adopted, as a measure of chemical affinity (for example, at constant pressure and constant temperature), the maximum useful work corresponding to one run of the reaction ( $\Delta \xi = 1$ ). This work equals the loss in G (i.e.,  $-\Delta G_{T,P}$ ) found on the condition that the chemical potentials are constant. The de Donder affinity differs from the classical affinity in approximately the same manner as the true reaction rate (the derivative) differs from the average rate (the difference quotient). Further we introduce the time factor and determine the reaction rate in the entire system according to de Donder (1937):

$$w_{T, P} = d\xi/dt \tag{14.15}$$

It should be noted that this definition of the reaction rate differs

from the definitions commonly used in kinetics [i.e., (1.4) or (1.5)] also by permitting both positive and negative values for the rate. Now, on the basis of Eqs. (14.13) and (14.15), we can write

$$dQ'/dt = A (d\xi/dt) = A\omega \geqslant 0 \tag{14.16}$$

and derive the following general conclusions as to the relation between affinity and rate: (1) if A > 0, then  $w \ge 0$ ; (2) if A < 0, then  $w \le 0$ ; (3) if A = 0, then w = 0.

Thus, with positive affinity the rate is either positive, which means that the reaction considered proceeds from left to right at a finite rate, or w=0 and the reaction is kinetically retarded but may proceed in the indicated direction in the presence of a suitable catalyst. In the second case (A < 0) the reaction takes place with a finite velocity from right to left or is again kinetically retarded (w=0); the latter case evidently corresponds to equilibrium and cannot include the relation A=0,  $w\neq 0$ , i.e., a finite rate at equilibrium.

Taking cognizance of Eq. (14.16) and also of Eq. (14.7), we can write

$$T(d_i S/dt) = T\sigma_{\text{chem}} = A\omega \geqslant 0$$
 (14.17)

Here use is made of the earlier introduced (14.8) concept and notation—the rate of appearance of entropy  $(d_iS/dt = \sigma_{\rm chem})$  in the system. The subscript "chem" points to the cause of the appearance of entropy—the only non-equilibrium process in this case is a chemical reaction. Expression (14.17) is represented in the form which is generally typical for the thermodynamics of non-equilibrium processes, namely: the rate of appearance of entropy multiplied by the absolute temperature  $(T\sigma)$  is equal to the product of a certain generalized force (A) by the generalized flux caused by it  $(\omega)$ .

In the subsequent treatment we shall deal with the rate of appearance of entropy in unit volume of the system, retaining the former symbol  $\sigma$ , which referred earlier to the system as a whole, and adding only the subscript V. In the simplest case of a homogeneous system  $\sigma_V = (1/V) (d_i S/dt)$ . If the only non-equilibrium process that takes place in the system is a chemical reaction, then, according to Eq. (14.17), we can write:

$$\sigma_{V \text{ (chein)}} = A \left( w_V / T \right) \geqslant 0 \tag{14.18}$$

where A is the affinity of the given reaction and  $w_V$  is the rate per unit volume, i.e.,  $w_V = (1/V) d\xi/dt$  if  $\xi$  is a chemical variable, and V is the volume of the system. However, there may simultaneously occur several, say r, reactions. Then expression (14.18) should be generalized:

$$\sigma_{V \text{ (chem)}} = \sum_{r} \left( A_r w_{V_r} / T \right) \geqslant 0 \tag{14.19}$$

where the sum is extended over all reactions.

The most remarkable feature of inequality (14.19) is that the sum  $A_r w_{V_r}$  must be positive for all reactions. At the same time, the separate terms of the sum, say  $A_l w_{V_l}$ , may be negative as well provided that the sum of the remaining terms is large enough to provide the conditions (14.19). In this way there arises the idea of the possible connection between the fluxes. In chemistry, this manifests itself in the phenomenon of induced or coupled reactions which proceed with a negative affinity, i.e., under the conditions of the constancy of T and P—with increasing Gibbs free energy. Thus, for instance, the synthesis of urea from carbon dioxide and ammonia (A < 0) takes place in the organism due to the breakdown of glucose ( $A \gg 0$ ) in the liver.

Other non-equilibrium processes, i.e., those occurring at a finite velocity, say, heat transfer, diffusion, etc., could be treated in an analogous manner. Here, according to the second law of thermodynamics, the rate of entropy appearance in general is

$$\sigma_{\mathcal{S}} \geqslant 0 \tag{14.20}$$

This law, however, does not require that each term in  $\sigma_s$  be positive. The coupling of non-equilibrium processes may lead to the appearance of negative terms in the sum, i.e., to phenomena that create situations of opposite direction as compared with those characteristic of a given isolated phenomenon. Thus, generally speaking, the concentration gradient must be equilibrated, but during the coupling of non-equilibrium processes the concentration gradients may be developed.

Let us designate the affinity or the generalized forces by  $X_i$ , and the fluxes by  $J_i$ . Then, Eq. (14.19) assumes the following general form:

$$T\sigma_{\mathcal{S}} = \sum_{i} I_{i} X_{i} \geqslant 0 \tag{14.21}$$

The possibilities of thermodynamics are, properly speaking, exhausted by writing this equation. The further use of Eq. (14.21) is connected with the assumptions as to the character of the dependence of fluxes on acting forces, these assumptions lying beyond the scope of thermodynamics. The situation here resembles, to a certain extent, the situation observed in classical thermodynamics when quite exact equations following from general laws can be employed in practice in combination with any equation of state, say, PV = nRT.

The sought-for relations  $J_i = f(X_i)$  are not known in a general

form. Therefore, one usually takes into account that at equilibrium there are no fluxes and the acting forces are equal to zero, and expands the function into a Maclaurin's series; for example,

$$J_{i} = I(X_{i}) = I(0) + X_{i} \frac{f'(0)}{1!} + X_{i}^{2} \frac{f''(0)}{2!} + \dots$$
 (14.22)

Here, in accordance with what has been said above, f(0) = 0. If we agree on the study of a system at equilibrium in a state not too remote from the state of equilibrium  $(X_i)$  is small), we may limit ourselves to a linear term of the series.

Further, we have to take account of the repeatedly mentioned possibility of existence of constraints between the various fluxes and eventually postulate such a linear relation between the fluxes  $J_i$  and the forces operating in the system:

$$J_i = \sum_{k=1}^n L_{ik} X_k \tag{14.23}$$

Here the summation which expresses the dependence of  $J_i$  for a given flux is carried out over all the non-equilibrium processes. Relation (14.23) is usually called the Onsager equation (1931). In accordance with what has been said above, this equation holds for the so-called *linear region* of non-equilibrium thermodynamics, i.e., for systems, the states of which differ little from equilibrium states.

Another relation—the famous Onsager reciprocal theorem—states that within the range of validity of the linear approximation the proportionality factors—the Onsager phenomenological coefficients  $L_{ik}$ —must satisfy the symmetry condition \*

$$L_{ik} = L_{ki} \tag{14.24}$$

There exist the proofs of the Onsager rule, which rely on the principle of microscopic reversibility and on the interpretation of the appearance and disappearance of fluctuations by means of the method of statistical mechanics (Prigogine, 1967). However, we cannot know a priori that all the cross coefficients  $L_{ik}$  do really exist. In fact, the presence of effective constraints between two non-equilibrium processes can be established only by means of experiments. But if the existence of a relation between the given force  $X_k$  and the flux  $J_i$  is experimentally established, then, according to the Onsager relation, there will also exist the reverse relation—between the force  $X_i$  and the flux  $J_k$ .

<sup>\*</sup> Apart from the Onsager phenomenological coefficients defined here, which are characteristic of the most widespread forces of the  $\alpha$ -type; the less frequently encountered forces of the  $\beta$ -type are characterized by the Kazimir coefficients. For these, relation (14.24) turns into the antisymmetric relation  $L_{ik} = -L_{kl}$ .

On the other hand, there exists a criterion which enables us to decrease a priori the number of effective constraints. This is the Curie principle of symmetry. It states that a macroscopic phenomenon in the system never has more elements of symmetry than the factor that has given rise to it. For example, the chemical affinity (which is a scalar) cannot cause a vectorial heat flux and the corresponding coupling factor disappears. What has been said corresponds to the following theorem: a constraint is possible between phenomena having identical tensor symmetry. However, according to Glansdorf and Prigogine (1970), the requirement of symmetry with respect to the constraints between non-equilibrium processes becomes invalid in the so-called linear region, i.e., beyond the range of applicability of Eq. (14.23) when processes and constraints that disturb symmetry become possible. We shall here confine ourselves to the linear region.

According to the experimental observations by Fourier, Fick, Ohm and others, each flux is proportional to the force coupled with it; the "direct" proportionality coefficient appearing here is denoted as  $L_{ii}$ . All such direct proportionality coefficients reveal themselves on the diagonal of the force matrix of a series of equations (14.23). This equation, however, contains the statement that the flux  $J_i$  can also be caused by the force  $X_k$  if the cross coefficient  $L_{ik}$  ( $i \neq k$ ) is different from zero.

As a whole, the linear law is valid for sufficiently slow processes when the system is not too far from the state of equilibrium. However, the range of phenomena covered by the phenomenological equations is still very wide; it includes many processes studied by physics, chemistry, biology and physiology.

To illustrate the applications of Eqs. (14.22) and (14.23), let us examine two simultaneous non-equilibrium processes, the phenomenological equation for which may be written as follows:

$$J_1 = L_{11}X_1 + L_{12}X_2 \tag{14.25}$$

$$J_2 = L_{21}X_1 + L_{22}X_2 \tag{14.26}$$

If these processes are thermal conduction and diffusion, then the factor  $L_{ik}$  is associated with thermodiffusion, i.e., with the manifestation of a concentration gradient in an initially homogeneous gaseous medium under the influence of a temperature gradient.

Expression (14.22) for the rate of appearance of entropy, which corresponds to the two processes, has the form

$$\sigma_{S} = T^{-1} \left\{ L_{11} X_{1}^{2} + \left( L_{12} + L_{21} \right) X_{1} X_{2} + L_{22} X_{2}^{2} \right\} \geqslant 0$$
 (14.27)

The inequality (14.27) can be satisfied, in a general case, with the following values of the phenomenological coefficients:

$$L_{11} > 0, \quad L_{22} > 0$$
 (14.28)

and

$$(L_{12} + L_{21})^2 < 4L_{11}L_{22} (14.29)$$

Thus, the "direct" coefficients are positive and the cross coefficients  $L_{12}$  and  $L_{21}$  may be either positive or negative, and their absolute value is limited by relation (14.29). All this corresponds to experimental data, according to which coefficients of the type of heat conductivity and electrical conductivity are always positive, while thermodiffusion coefficients, for example, have no definite sign.

Of special interest to us is the question of the applicability of linear phenomenological laws in chemical kinetics. We shall write an elementary reaction in a general form:

$$v_1B_1 + v_2B_2 + \dots \xrightarrow{k} v_1'B_1' + v_2'B_2' + \dots$$

where k and k' are the rate constants of the forward and reverse reactions. Let us denote the molar concentrations and stoichiometric coefficients of all the participants of the reaction by the symbols  $c_{\gamma}$  and  $v_{\gamma}$ ; the corresponding quantities for the reactants are  $c_i$  and  $v_i$ , and those for the products,  $c_j$  and  $v_j$ . Thus, for example, we may write the following relationships:

$$\prod_{\mathbf{v}} c_{\mathbf{v}}^{\mathbf{v}_{\mathbf{v}}} = \prod_{i} c_{i}^{\mathbf{v}_{i}} / \prod_{i} c_{i}^{\mathbf{v}_{i}}$$
(14.30)

Further, proceeding from the basic law of kinetics, we write the reaction rate:

$$w_V = k \prod_i c_i^{\nu_i} - k \prod_j c_j^{\nu_j} = \stackrel{\rightarrow}{w} \left( 1 - \lambda \prod_{\gamma} c_{\gamma}^{\nu_{\gamma}} \right)$$
 (14.31)

where  $\overset{>}{w} = k \prod c_i^{v_i}$  is the rate of the forward reaction and  $\lambda \equiv k'/k$ . Now, using the van't Hoff isotherm equation, we write the affinity of the reaction:

$$A = -\sum_{\mathbf{v}} \mathbf{v}_{\mathbf{v}} \mu_{\mathbf{v}} = RT \ln \left( K_c / \prod_{\mathbf{v}} c_{\mathbf{v}}^{\mathbf{v}_{\mathbf{v}}} \right)$$
 (14.32)

Here, obviously,

$$RT \ln K_c = -\sum_{\gamma} \nu_{\gamma} \mu_{\gamma}^0 \tag{14.33}$$

if  $\mu_{\gamma}^{0'}$ s are the chemical potentials in the standard state, which are dependent only on temperature for ideal-gas mixtures and, in addition, on pressure for ideal solutions.

Introducing now the affinity A from Eq. (14.32) into the rate equation, we obtain a general relation between reaction rate and affinity for ideal-gas mixtures and dilute solutions, which holds for any non-equilibrium state:

$$w_V = \stackrel{\rightarrow}{w} \left[ 1 - \lambda K_c \exp\left( - \left( A/RT \right) \right] \right]$$
 (14.34)

However, on the condition of equilibrium  $w_V = 0$  and A = 0, from Eq. (14.34) it is easy to see that  $k/k_1 = 1/\lambda = K_c$ , and the rate equation assumes the form

$$w_V = \overset{\Rightarrow}{w} \left[ 1 - \exp\left( - A/RT \right) \right] \tag{14.35}$$

which is also valid for any non-equilibrium state. The exponential function may be expanded into a Taylor series:

$$1 - e^{-A/RT} = \frac{A}{RT} - \frac{1}{2!} \left(\frac{A}{RT}\right)^2 + \frac{1}{3!} \left(\frac{A}{RT}\right)^3 + \dots$$
 (14.36)

If the reacting system approaches the state of equilibrium and the affinity is small, so that

$$|A/RT| \ll 1 \tag{14.37}$$

we may retain only the first term in the series and write the reaction rate in the form

$$w_V = \stackrel{\rightarrow}{w}_0 (A/RT) \tag{14.38}$$

Here, since in the Taylor series we retained only the first term, which is valid for small values of affinity, it then follows that the reaction rate  $w_0$  too refers to a point close to w=0, A=0, i.e., to the state of equilibrium, which is why it is labeled  $w_0$ . In other words,  $w_0$  is the rate of the forward reaction at equilibrium, i.e.,  $w_0 = k \prod_i \bar{c}_i^{v_i}$ , where  $\bar{c}_i$ s are the equilibrium concentrations of the reactants.

Thus, instead of Eq. (14.35), we obtain the relation

$$w_V = (\overset{\rightarrow}{w_0} / RT) A = LA \tag{1.1.39}$$

which may be regarded as a phenomenological law of the type (14.23), which is valid in this particular case for ideal-gas systems and in infinitely dilute solutions under the conditions close to equilibrium. The phenomenological coefficient is defined in this case by the relation

$$L = (\overset{\Rightarrow}{w}_0 / RT) \tag{14.40}$$

From the foregoing it must be clear that the coefficient L is invariably positive, depends on temperature, on the amount and activity of the catalyst, and is determined by the equilibrium concentrations  $\bar{c}_i$  of the reactants since these determine the rate  $w_0$ . It should be emphasized once again that  $\bar{w}$  differs from the overall rate  $w_V$  (14.31), which is dependent on the instantaneous values of the concentrations of all the participants of the reaction.

Thus, it seems as if we obtained the condition of the applicabi-

lity of the linear phenomenological law to chemical reactions—the closeness of the system to the state of equilibrium. This, of course, would have restricted the applicability of non-equilibrium thermodynamics to chemical reactions. However, as will be shown below, the situation will not be so hopeless if the reaction can be represented as proceeding in several elementary steps.

But let us first consider the other extreme case, namely

$$A/RT \longrightarrow \infty$$
 (14.41)

Then the exponential function B (14.25) turns to zero and  $w_v = w_0$ , i.e., the reaction rate is no longer dependent on affinity. It may be said that this corresponds to the effect of saturation with respect to the affinity, and in the region where this effect is manifested, the rate of appearance of entropy becomes a linear function of affinity in conformity with Eqs. (14.17) and (14.18).

Let us now discuss the occurrence of several reactions in a single phase. Here, as it turns out, two cases should be distinguished. In the first, the number of elementary reactions is equal to the number of linearly independent reactions. Then, relations (14.38) and (14.39) may be written for each elementary reaction, and for each of them there can be found unambiguous values of the quantities w, k, k', A and  $K_c$  with the appropriate subscripts. In this simpler case there arises no coupling between the reactions.

In the second case, the number of elementary reactions is larger than the number of linearly independent reactions so that formally some of the reaction equations can be obtained by way of a linear combination of the other equations. Then, as it turns out, the relations  $k/k_1 = K_c$  and  $w = w (1 - e^{-A/RT})$  cannot be derived from the basic kinetic law and the thermodynamic equilibrium conditions alone. In this case there arises a connection between the reactions.

Let us return to the first case and consider first two consecutive reactions, represented by linearly independent equations and, hence, not interconnected; these reactions are the elementary processes as well: (1) B = C, (2) C = D. These may be, for example, the isomerization reactions: o-xylene = m-xylene, and m-xylene = p-xylene. Both these reactions are really reversible, have been studied in a dilute solution of xylene in toluene in the presence of  $AlCl_3$  and HCl. No direct conversion of o-xylene to p-xylene and vice versa takes place. Therefore, linear combinations are excluded.

Under conditions close to equilibrium we may first write the following relations for these reactions:

$$|A_1/RT| \ll 1, \quad |A_2/RT| \ll 1$$
 (14.42)

and, second, the phenomenological laws

$$w_1 = L_{11}A_1, \quad w_2 = L_{22}A_2 \tag{14.43}$$

Here the direct phenomenological coefficients

$$L_{11} = \stackrel{\rightarrow}{w_{01}}/RT$$
 and  $L_{22} = \stackrel{\rightarrow}{w_{02}}/RT$  (14.44)

contain the quantities  $\overset{\Rightarrow}{w}_{01}$  and  $\overset{\Rightarrow}{w}_{02}$ , i.e., the rates of the forward elementary reactions  $B \rightleftharpoons C$  and  $C \rightleftharpoons D$  at equilibrium. When considering relations (14.44) one may notice that the cross coefficients are equal to zero, i.e.,  $L_{12} = L_{21} = 0$  and no connection between reactions 1 and 2 is present. The situation, however, is changed if we assume the possibility of the direct conversion  $B \rightleftharpoons D$ .

We shall now consider, in a similar manner, a sequence of consecutive reactions according to Prigogine:

$$(2) \quad C \longrightarrow D$$

Assuming that the following conditions

$$|A_i/RT| \ll 1$$
  $(i = 1, 2, ..., r)$  (14.45)

are satisfied, we write phenomenological laws of the type (14.38):

$$w_{Vi} = L_{ii}A_i$$
 (*i* = 1, 2, ..., *r*) (14.46)

corresponding to the general linear relations provided that the reactions are not interconnected, i.e., when  $L_{ij} = 0$  for i = j.

An interesting result can be obtained if the separate elementary reactions 1, 2, r are not considered. For example, they may be unknown. Then, for the conversion  $B \rightleftharpoons Y$  we may introduce the total affinity A and the rate  $w_V$ . As can easily be seen from the definition of the affinity of reaction i

$$A_i = -\sum_{\mathbf{v}} \mathbf{v}_{\mathbf{v}^i} \mathbf{\mu}_{\mathbf{v}} \tag{14.17}$$

the total affinity is equal to the sum of  $A_i$  for the elementary reactions:

$$A = A_1 + A_2 + \dots + A_r \tag{14.48}$$

If the intermediates C, D ... X are unstable, say, are free radicals and atoms, then, according to the quasi-steady-state method, we may write:

$$w_{V1} = w_{V2} = \dots = w_{Vr} = w_V \tag{14.49}$$

where  $w_{\nu}$  is the observed reaction rate.

From relations (14.46) and (14.49) we obtain  $w_V = L_{11}A_1 = L_{22}A_2 = \ldots = L_{rr}A_r$ . Now from Eq. (14.48) it follows that

$$A = A_1 + A_2 + \dots + A_r = \frac{w_V}{L_{11}} + \frac{w_V}{L_{22}} + \dots + \frac{w_V}{L_{rr}} = w_V \sum_{1}^{r} \frac{1}{L_{ii}}$$

If we introduce the notation  $\sum (1/L_{ii}) = 1/L$ , then we can write  $w_V = LA$  (14.50)

Thus, the measured overall reaction rate  $w_V$  is found to be proportional to the affinity A of the overall reaction  $B \rightleftharpoons Y$ ; here it is essential that the relation  $|A/RT| \ll 1$  may be left unfulfilled if only the conditions (14.45), i.e.,  $|A_i/RT| \ll 1$ , are valid. It turns out in practice that quite a number of reactions, including catalytic reactions, which proceed by a complicated mechanism satisfactorily obey the law (14.50).

As an example, we shall give the catalytic dehydrogenation of cyclohexane or the hydrogenation of benzene in a gaseous medium:

$$C_6H_{12} \longrightarrow C_6H_6 + 3H_2$$

which has been studied by Prigogine, Outer and Herbo. The catalyst used has the following composition: 50 mol. % Ni, 25 mol. % ZnO, 25 mol. %  $Cr_2O_3$ ; the initial pressures in the experiments were identical and the temperatures varied from 500 to 582 K. It was found that the reaction rate (g/hr) is linearly dependent on the ratio A/R in the ranges studied (from -1000 to +600 K). Thus, the linear law is fulfilled within the range of A/RT from -2 to +1, which confirms what has been said above.

# SUGGESTIONS FOR FURTHER READING

- 1. Benson, S. W., The Foundations of Chemical Kinetics, McGraw-Hill Book Company, New York, 1960.
- 2. Boldyrev, V. V., The Effect of Defects in Crystals on the Rate of Decomposition of Solids, Tomsk, Tomsk University Press, 1963 (in Russian).
- 3. Caldin, E. E., Fast Reactions in Solution, Blackwell Scientific Publications, Ltd., Oxford, 1964.
- 4. Calvert, J. and J. Pitts, *Photochemistry*, New York-London-Sydney, 1966.
- 5. Chemical Kinetics and Chain Reactions, Nauka, 1966 (in Russian).
- 6. Cundall, R. B. and A. Gilbert, *Photochemistry*, Appleton-Century-Crofts, New York, 1970.
- 7. Emanuel, N. M. and D. T. Knorre, A Course of Chemical Kinetics, Moscow, Vysshaya shkola, 1974 (in Russian).
- 8. Frost, A. A. and R. G. Pearson, Kinetics and Mechanism, 2nd ed., John Wiley and Sons, Inc., New York, 1961.
- 9. Garner, W. E. (ed.), *Chemistry of the Solid State*, Butterworth and Co. (Publishers), Ltd., London, 1955.
- 10. Glasstone, S., Theoretical Chemistry, New York, 1948.
- 11. Glasstone, S., K. J. Laidler, and H. Eyring, The Theory of Rate Processes, McGraw-Hill Book Company, 1941.
- 12. Glorkler, G. and C. Lind, The Electrochemistry of Gases and Other Dielectrics, John Wiley and Sons, 1939.
- 13. Heterogeneous Chemical Reactions. Edited by M. M. Pavlyuchenko, Minsk, Izd. MVO BSSR, 1961.
- 14. Hinshelwood, C. N., Kinetics of Chemical Change, Clarendon Press, Oxford, 1940.
- 15. Kassel, L. S., The Kinetics of Homogeneous Gas Reactions, Reinhold, New York, 1932.
- 16. Kobozev, N. I. et al., Zhur. Fiz. Khim., 4, 975, 406 (1933); 14, 1550 (1940); 15, 882 (1941).
- 17. Kondratiev, V. N., Kinetics of Chemical Gas Reactions, Izd. Akad. Nauk SSSR, Moscow, 1958 (an English translation, in two volumes, has been issued by the U. S. Atomic Energy Commission; a second translation, edited by N. B. Slater, has been published by the Pergamon Press, Oxford, 1964).
- 18. Moelwyn-Hughes, E. A., The Kinetics of Reactions in Solution, Clarendon Press, Oxford, 1947.
- 19. Noyes, W. A., and A. Leighton, *Photochemistry of Gases*, Reinhold Publishing Corporation, 1941.
- 20. Rozovsky, A. Ya., Kinetics of Topochemical Reactions, Moscow, Khimiya, 1974 (in Russian).
- 21. Semenov, N. N., Chemical Kinetics and Chain Reactions, Clarendon Press, Oxford, 1935.

- 22. Semenov, N. N., Some Problems in Chemical Kinetics and Reactivity, Moscow, 1954 (two English translations are available: one by M. Boudart, Princeton University Press, Princeton, N. J., 1958; one by J. E. S. Bradley, Pergamon Press, London, 1958).
- 23. Shilov, N., Induced Oxidation Reactions, Moscow, A. I. Mamontov Publishing Company, 1905 (in Russian).
- 24. Slater, N. B., Theory of Unimolecular Reactions, Cornell University Press, Ithaca, N. Y., 1959.
- 25. Spitalsky, E., Über die kinetischen Gesetze der homogenen Katalyse. Z. f. Physikalisch. Ch., 122, 1257-86, 1926.
- 26. Terenin, A. N., The Photochemistry of Dyes, Moscow, Izd. Akad. Nauk SSSR. 1947 (in Russian).
- 27. Trotman-Dickenson, A. F., Gas Kinetics, Butterworth and Co. (Publishers), Ltd., London, 1955.
- 28. Vasiliev, S. S., Zhur. Fiz. Khim., 26, 1027, 1198 (1952); 27, 1081, 1410 (1953);
- 33, 1100 (1959); 34, 2174 (1960); 38, 2214 (1964).
  29. Yeremin, E. N., The Elements of Gas Electrochemistry, Izd. MGU (Moscow State University Press), 1968 (in Russian).
- 30. Young, D., Decomposition of Solids, Oxford, 1966,

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